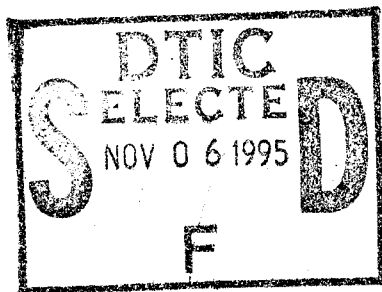


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INTERNATIONAL CONFERENCE

NANO-STRUCTURES AND
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IN POLYMER SYSTEMS

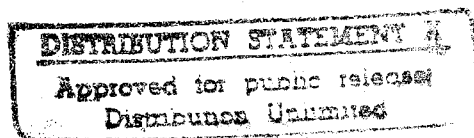
St.-Petersburg - Moscow
May 18 - 26, 1995

Program and Abstracts

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Russian Academy of Sciences
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Time schedule of the conference

19.05.95

Opening of the conference and Session 1	18.00 - 20.00
Departure from St.Peterburg	20.00
Welcome Dinner	20.30

20.05.95

Breakfast	07.15 - 08.00
Valaam, Excursion	08.00 - 14.00
Lunch	14.00 - 15.00
Session 2	15.00 - 17.00
Coffee break	17.00 - 17.30
Session 3	17.30 - 19.50
Dinner	19.50 - 20.50
Poster session 1	20.50 - 22.50

21.05.95

Breakfast	08.15 - 09.00
Session 4	09.00 - 11.00
Coffee break	11.00 - 11.30
Session 5	11.30 - 13.30
Lunch	14.00 - 15.00
Kizhi, Excursion	16.00 - 20.00
Dinner	20.00 - 21.00

22.05.95

Breakfast	08.15 - 09.00
Session 6	09.00 - 11.00
Coffee Break	11.00 - 11.30
Session 7	11.30 - 13.30
Lunch	13.30 - 14.30
Poster Session 2	15.00 - 17.00
Session 8	17.00 - 19.00
Dinner	20.00 - 21.00

23.05.95

Breakfast	08.15 - 09.00
Belozersk, Excursion	09.00 - 14.00
Lunch	14.00 - 15.00
Session 9	15.30 - 17.30
Coffee Break	17.30 - 18.00
Session 10	18.00 - 19.40
Dinner	20.00 - 21.00

24.05.95

Breakfast	08.15 - 09.00
Uglich, Excursion	09.00 - 13.00
Lunch	13.00 - 14.00
Session 11	14.00 - 16.00
Coffee Break	16.00 - 16.30
Session 12	16.30 - 17.50
Green Stop in Sosenky	18.00 - 20.00
Conference Dinner	20.00

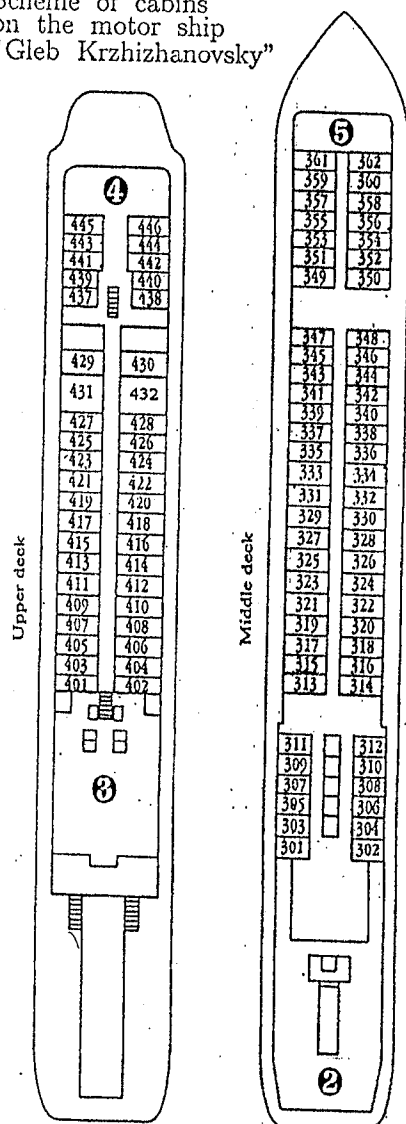
25.05.95

Breakfast	08.15 - 09.00
Session 13	09.00 - 11.00
Coffee Break	11.00 - 11.30
Session 14	11.30 - 13.30
Lunch	13.30 - 14.30
Session 15	15.00 - 16.20
Coffee Break	16.20 - 16.50
Session 16	16.50 - 17.50
Closing of the conference	17.50 - 18.20
Dinner	18.30 - 19.30
Arrival to Moscow	20.00

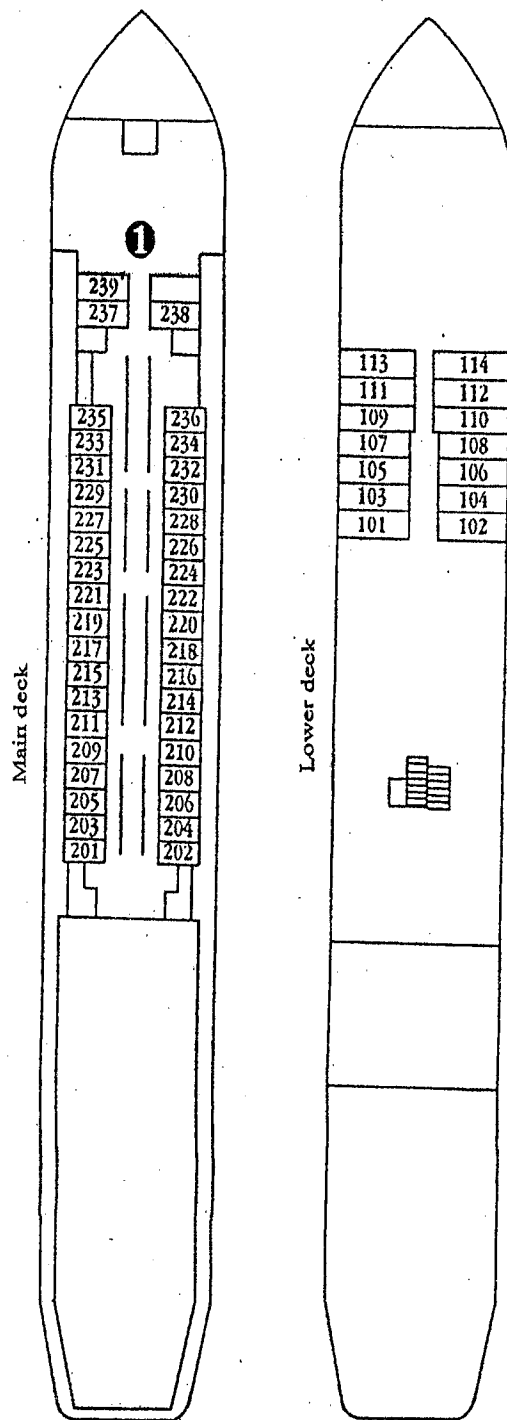
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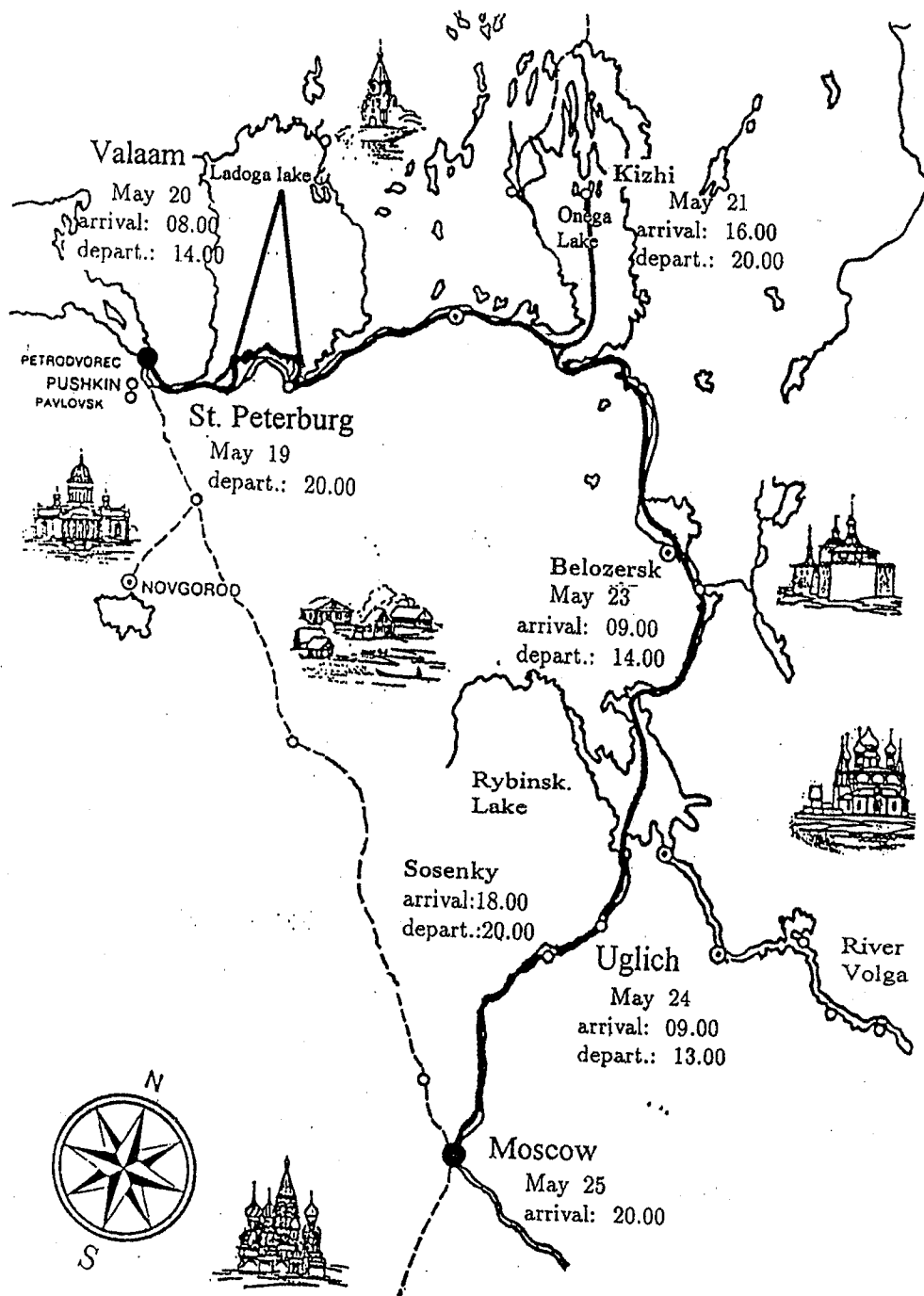
Breakfast	08.15 - 09.00
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Scheme of cabins
on the motor ship
"Gleb Krzhizhanovsky"



- 1 Reception
- 2 Restaurant
- 3 Bar
- 4 Musical Room
- 5 Reading Room
- Organizing Committee - Cabin 431
- Medical Help - Cabin 205





SCIENTIFIC PROGRAM

FRIDAY, 19 MAY

18.00 OPENING OF THE CONFERENCE

LECTURE SESSION 1

(Chairman - V.A.Kabanov)

18.40-20.00

PL1 Plenary lecture

18.40 E.Baer

Hierarchical Structures in Nano-Layered Polymeric Systems

PL2 Plenary lecture

19.20 G.Wegner

Shape Persistent Macromolecules as Building Units of
Complex Supramolecular Architectures

SATURDAY, 20 MAY

LECTURE SESSION 2

(Chairman - T.Nose)

15.00 - 17.00

PL3 Plenary lecture

15.00 B.Chu, C.Wu

Coil-Globule Transition: Self-Assembly of a Single
Polymer Chain

Oral lectures:

OL1 K.A.Dawson, E.Timoshenko, Y.Kuznetzov

15.40 Kinetics of Conformational Change of Polymers Coil-to-
-Globule Transition

OL2 A.Yu.Grosberg, V.S.Pande, T.Tanaka

16.00 How to Design Heteropolymer with a "Smart" Sequence?

OL3 I.Ya.Erukhimovich

16.20 Macro- and Microphase Separation in Polymer Solutions in
Nearly Critical Low-Molecular Solvents

- OL4 V.L.Bodneva, I.P.Borodin, T.N.Khazanovich
16.40 Internal Hydrodynamics of Polymer Coils or Spherically
Symmetric Aggregates in Dilute Solutions

LECTURE SESSION 3

(Chairman - V.A.Davankov)

17.30 - 19.50

Oral lectures:

- OL5 J.Blackwell, Y.K.Kwon, S.N.Chvalun, C.A.Danko, V.Percec,
17.30 J.A.Heck
X-ray Analyses of the Supramolecular Tubular Structures
Formed by a Poly(methacrylate) with Highly Tapered Side
Groups
- OL6 A.A.Askadskii
17.50 Computer Design, Synthesis and Investigation of Gradient-
Modulus Polymers
- OL7 H.-J.Cantow, D.Brizzolara, L.Schulz, A.J.Domb
18.10 Biodegradable Stereocomplexes and Block Copolymers -
Strategies for Novel Interfaces
- OL8 A.D.Litmanovich, N.A.Plate
18.30 A Control of Primary Structure in the Products of
Macromolecular Reactions
- OL9 L.M.Bronstein, P.M.Valetsky, S.P.Solodovnikov,
18.50 R.A.Register
Nanodispersed Metal and Metal Oxides Particles in
Polymeric Matrices from Polyacrylonitrile Precursors
- OL10 G.B.Sergeev, I.A.Gromchenko, V.V.Zagorsky, M.A.Petrukhina,
19.10 B.M.Sergeev
Nanosize Metal Clusters in Polymer Systems

- OL11 A.M.Muzafarov, E.A.Rebrov, G.M.Ignat'eva, N.G.Vasilenko
19.30 New Synthetical Approaches to Organosilicon Polymers of
Dendritic Structure.

POSTER SESSION 1

20.50-22.50

- P1 L.I.Valuev
The Specific Features of Conformational Behavior of
Physiologically Active Polymers
- P2 S.M.Mel'nikov, V.G.Sergeyev, Kenichi Yoshikawa
Discrete Coil-Globule Transition of Single Large DNA
Molecules Induced by Cationic Surfactant
- P3 S.Kidoaki, K.Yoshikawa
Collapsed Single DNA Chain Memorizes the Past in its
Higher Order Structure
- P4. A.P.Safronov, A.A.Tager, E.V.Korolyova
Association and Solvation in the Process of Dissolution
of Poly(acrylic acid) in Water and Non-aqueous Solvents
- P5 M.Vigouret, M.Rinaudo, R.Borsali
Static and Dynamic Light Scattering Measurements on Dilute
Solutions of Methylcellulose as a Function of Temperature
- P6 V.Prevysh, Bo-Chy Wang, R.J.Spontak
Influence of Salting-in Effects on the Properties and
Stability of Hydrogen-Bonded Interpolymer Complexes
- P7 J.R.Ilzhoefer, Brian C.Broom, R.J.Spontak, S.A.Khan,
E.A.Vogler
Block Copolymer Gels: a New Family of Thermotropic
Thixotropes
- P8 A.Yu.Grosberg, A.Feigel, Y.Rabin
Flory Type Theory for Swelling and Collapse of a Knot

- P9 K.N.Bakeev, E.A.Lysenko, Y.N.Viteuk, A.B.Zezin,
V.A.Kabanov
Polymer-Surfactant Complexation in Aqueous Solutions of
Hydrophobically Modified Polycations and Vesicles of
Various Surfactants.
- P10 K.N.Bakeev, Y.M.Shu, A.V.Lezov, A.B.Mel'nikov,
I.P.Kolomiets, E.I.Rjuntsev, A.B.Zezin, W.J.MacKnight,
V.A.Kabanov
New Nonstoichiometric (Polyelectrolyte-Surfactant)
Complexes Soluble in Low-Polarity Solvents.
- P11 A.V.Lezov, A.B.Mel'nikov, K.N.Bakeev, E.A.Lysenko,
E.I.Rjuntsev
Hydrodynamical, Dynamo- and Electrooptical Characteristics
of Ionomer-Surfactant Complexes in Nonopolar Solvent.
- P12 K.N.Bakeev, E.A.Ponomarenko, T.V.Shishkanova, D.A.Tirrell,
A.B.Zezin, V.A.Kabanov
Self-Assembly in Aqueous Solutions of Amphiphilic
Polycations and Surfactants of the Same Charge.
- P13 D.V.Pergushov, V.A.Izumrudov, A.B.Zezin, V.A.Kabanov
A Study of Cation and Anion Effects on the Stability and
Behavior of Water-Soluble Interpolyelectrolyte Complexes.
- P14 A.V.Lezov, A.B.Mel'nikov, I.P.Kolomiets, K.N.Bakeev,
A.B.Zezin, E.I.Rjuntsev
Hydrodynamical, Dynamo- and Electrooptical Properties of
Polyelectrolyte-Surfactant Complexes in Chloroform.
- P15 P.G.Khalatur, A.R.Khokhlov, I.A.Nyrkova, A.N.Semenov
Non-Spherical Micelles in Solutions of Polymers with
Strongly Interacting Groups: Computer Simulations.
- P16 Le Thi Minh Thanh, E.E.Makhaeva
Effect of Surfactants on the Swelling Behavior of the
Polyampholyte Gels.

- P17 E.E.Makhaeva, Le Thi Minh Thanh, S.G.Starodubtsev.
The Swelling Behavior of Poly(vinylcaprolactam) Gels in Aqueous Solutions.
- P18 N.P.Shusharina, I.A.Nyrkova, A.R.Khokhlov.
Micelles in Solutions of Charged Diblock Copolymer in Selective Solvents.
- P19 E.Yu.Kramarenko, A.R.Khokhlov.
Phase Transition Behavior of Polyelectrolyte Gels With Variable Degree of Ionization.
- P20 O.E.Philippova, N.S.Karibyants, S.G.Starodubtsev.
Interaction of Poly(methacrylic acid) Hydrogels with Poly(ethylene glycol).
- P21 N.S.Karibyants, O.E.Philippova, S.G.Starodubtsev.
Poly(methacrylic acid) Hydrogels - Nonionic Surfactant Complexes.
- P22 S.G.Starodubtsev, A.R.Khokhlov, F.Yeh, E.L.Sokolov, B.Chu
Interaction of Slightly Cross-Linked Poly(diallidimethylammonium chloride) Gels with Inorganic Salts and Surfactants. Phase Transitions and Structure of Complexes.
- P23 T.A.Larina, I.I.Vointseva
The Relation Between Size and Quantity of Microgel and the Conditions of Interpolymers Synthesis.
- P24 N.L.Sitnikova, O.E.Philippova, T.G.Pieper
Microheterogeneities in Collapsed Polyelectrolyte Gels.
- P25 K.I.Bolyachevskaya, A.A.Litmanovich, S.V.Markov, I.M.Papisov.
Interpolymer. Complexes and Composites Obtained by Matrix Polycondensation of Silica Acid.

- P26 E.Pashkovsky, T.Litvina
Behavior of Nematic Polymer Solutions Near the Nematic -
Smectic A Transition.
- P27 S.I.Belousov, E.Sautter, W.Pechhold, N.N.Makarova,
Yu.K.Godovsky
Self-Assembling in Thin Films of Mesophase Linear and
Cyclolinear Polysiloxanes
- P28 I.M.Dayletbaeva, P.A.Kirpichnicov, A.P.Rakhmatullina
Synthesis and Investigation of the Liquid Crystal
Polyurethane Metal Complexes.
- P29 B.Z.Volchek, D.A.Medvedeva, S.V.Shilov
Peculiarities of Liquid Crystalline Ordering in Melts of
Polymer with Different Chemical Structure.
- P30 V.I.Irzhak, M.L.Tai
Mathematical Models of Self-Assembly
- P31 G.V.Popova, V.V.Kireev, S.G.Yudin, S.P.Palto, H.Menzel,
Ande Lu
Study of Ordered Structures of L- α -polyglutamic Acid
Covalently Bonded with Different Dyes in LB-films.
- P32 N.A.Kalabina, S.Yu.Zaitsev, V.P.Zubov, E.P.Lukashev,
A.A.Kononenko
Polymer Ultrathin Films with Immobilized Photosynthetic
Reaction Center Proteins.
- P33 I.I.Vointseva, P.M.Valetsky, L.M.Gilman, Yu.P.Kudryavtsev
Carbonization of the Surface by Chemical
Dehydrochlorination of Poly-1,1,2-trichlorobutadiene.
- P34 A.P.Krasnov, L.B.Makina, S.Ju.Panov
Self-Organization of Nanometer Surface Layers During
Friction of Aliphatic Polymer.

- P35 V.M.Rudoy, V.A.Ogarev
Surface Dynamics of Photooxidized EPDM Rubber
- P36 Yu.Lyov, K.Ariga, T.Kunitake
Assembly of Multicomponent Protein Superlattices by Means
of Electrostatic Layer-by-Layer Adsorption.
- P37 V.V.Arslanov, L.S.Sheinina
Formation of Two-Dimensional Organic Networks on Liquid
Surfaces and Solid Substrates.
- P38 A.I.Dolinnyi
Model Calculations for the Growth of Surface Layers During
Spinodal Decomposition in Polymer Mixtures.

SUNDAY, 21 MAY

LECTURE SESSION 4

(Chairman - E.Meinecke)

09.00 - 11.00

- PL4 Plenary lecture
09.00 N.A.Plate
Self-Assembling with Formation of Mesomorphic Polymer
Structures in Non-Mesogenic Species
- PL5 Plenary lecture
09.40 A.Abe
Conformational Transitions and Incidental Reorganization
of Mesophase Structures Peculiar to Polyaspartates - a
Highly Versatile System Designed by Nature
- Oral lectures:
- OL12 Yu.K.Godovsky, N.N.Makarova
10.20 Self-Ordering in Cyclolinear Polyorganosiloxanes
- OL13 G.Scherowsky, A.Beer, U.Fichna, K.Grueneberg, U.Mueller
10.40 Electrooptical Properties of Novel Ferroelectric Liquid
Cristal Polymers

LECTURE SESSION 5

(Chairman - A.R.Khokhlov)

11.30 - 13.30

Oral lectures:

- OL14 D.V.Kuznetsov
11.30 Interface Effects in Nematic Liquid-Crystalline Structures of Polymer Solutions
- OL15 W.Gronski, Ch.Tefehne, J.Sanger, A.Martin
11.50 Amorphous-LC-Blockcopolymers. Synthesis, Morphology and Phase Behaviour
- OL16 A.Halperin, D.R.M.Williams
12.10 Liquid Crystalline Polymers in Nematic Solvents: Interfacial Properties
- OL17 T.Turunen, H.Tenhu, V.Timofeev, B.Samarianov
12.30 Aggregation and Gelation of Poly(octyl isocyanate) in Nonpolar Solvents
- OL18 G.S.Attard, M.Edgar, J.Glyde, C.Goeltner,
12.50 Synthesis of Mesoporous Polymers in Lyotropic Liquid -Crystalline Phases
- OL19 S.Valiyaveetil, V.Enkelmann, G.Moessner, C.Meiners,
13.10 L.Wang, M.Pfaadt, D.Pressner, H.W.Spiess, C.Gans, R.Gereke, M.Klapper, K.Mueller
Hydrogen Bonded Supramolecular Aggregates in the Solid Lattice and in the Mesophases

MONDAY, 22 MAY

LECTURE SESSION 6

(Chairman - H.Frisch)

09.00 - 11.00

- PL6 Plenary lecture
09.00 V.A.Kabanov
Molecular Recognition Phenomena in Polyelectrolyte Systems

PL7 Plenary lecture

09.40 A.Eisenberg

Morphological Versatility in the Self-Assembly of Block
Polyelectrolytes in Aqueous Environments

Oral lectures:

OL20 T.M.Birshtein, E.B.Zhulina, O.V.Borisov

10.20 Theory of Ionizable Polymer Brushes

OL21 K.Nishida, K.Kaji, T.Kanaya

10.40 Charge Density Dependence of Correlation Length in
Polyelectrolyte Solutions

LECTURE SESSION 7

(Chairman - A.Yu.Grosberg)

11.30 - 13.30

Oral lectures:

OL22 A.R.Khokhlov

11.30 Conformational Transitions in Polyelectrolyte Responsive
Gels

OL23 R.Audebert

11.50 Self Assemblies in Hydrophobically Modified
Polyelectrolytes

OL24 A.B.Zezin, V.A.Izumrudov, V.A.Kabanov

12.10 A Self-Assembly Phenomena in Multicomponent Systems
Composed of Polyelectrolytes and Ionic Surfactants

OL25 M.Antonietti, J.Conrad, A.Kaul, C.Burger

12.30 Polyelectrolyte-Surfactant Complexes: Highly Ordered
Microphase Separated Polymers

OL26 A.A.Darinskii, O.V.Borisov, E.B.Zhulina

12.50 Dynamics of Weakly Charged Polyelectrolyte in an
Elongational Flow. Effect of Solvent

- OL27 M. Shibayama
13.10 Microscopic Inhomogeneities in Weakly-Charged Temperature
 Sensitive Polymer Gels and Solutions

POSTER SESSION 2

15.00 - 17.00

- P39 V.K. Fedyanin, S.B. Solganik
 Dynamic and Thermodynamic Non-Linear Excitations on
 Polyacetylene, Polyene, AB-polymers.
- P40 I.I. Potemkin, S.V. Panyukov
 Spatial Structures Induced by Stretching of Entangled
 Networks.
- P41 E.E. Dormidontova, I.Ya. Erukhimovich, A.R. Khokhlov.
 Microdomain Structures in Polymer Solutions (Blends) Near
 Glass Transition Temperature.
- P42 A.Z. Akheyan, E.Sh. Mamasakhlisov, V.F. Morozov,
 N.E. Matevosian
 Spinodal Decomposition in Polymer Globule with Secondary
 Structure
- P43 V.F. Morozov, E.Sh. Mamasakhlisov, N.E. Matevossian
 Globular State of the Polymer Chain with Rigid Side Chains
 with the Quenched Disorder.
- P44 C. Burger, M. Antonietti, W. Ruland
 Cubic Phases in Block Copolymers: "Photo Structure",
 Structure, and Density Projection.
- P45 S.N. Chvalun, N.Ph. Bakeev, Y. Kwon, V. Percec, J. Blackwell
 Order-Disorder Transition in Self-Assembled Columnar Phase
 Formed by a Polymethacrylate with a Highly Tapered Side
 Chain and its Monomeric Precursor.

- P46 G.M.Gunyaev, T.G.Sorina
Fibrous Nanocomposites Based on Sic Whiskers
- P47 L.A.Zenitova, I.N.Bakirova, P.A.Kirpichnikov
The Polyurethane Isocyanurate Morphology
- P48 V.A.Ivanov, P.G.Khalatur, V.V.Vasilevskaya
Multiplets in Telechelic Polymer: Molecular Dynamics Simulation.
- P49 V.A.Ivanov, B.Jung, A.N.Semenov, I.A.Nyrkova, A.R.Khokhlov
Simple One-Particle Diffusional Model to Mimic Some Properties of the Glass Transition.
- P50 L.V.Men'shikova, B.N.Klyushnik, I.V.Talyzin, P.G.Khalatur
Monte Carlo Simulation of Large-Scale (Mesoscopic) Heterogeneities in Cross-Linked and Associative Networks.
- P51 M.A.Mazo, M.J.Kotelyanskii, E.F.Oleynik
Formation of "Free-Volume" Phase at Vittrification of 2D Lennard-Jones System. Computer Simulation.
- P52 V.S.Papkov, G.G.Nikiforova, V.G.Nikol'skii, I.A.Krasotkina, E.S.Obolonkova
Transparent Microheterogenous Blends of Multiblock Copolymers with Foreign Homopolymers
- P53 A.E.Likhtman, A.N.Semenov
The Theory of Superstructures in Block Copolymer System.
- P54 O.V.Borisov
Conformations of Star-Branched Polyelectrolytes
- P55 E.S.Nefed'ev, M.K.Kadirov, N.V.Chuikova
The Study of Nature of Thiokol-Epoxy Polymer and Brass Substrate Interphase Layer with EPR and Electron Spin Echo.

- P56 V.V.Yashin, E.N.Govorun, Ya.V.Kudryavtsev, A.D.Litmanovich
Macromolecular Reactions as a Tool to Control Polymer
Blend Structure: Simple Theoretical Models.
- P57 P.G.Khalatur, A.R.Khokhlov, V.V.Vasilevskaya
Formation of Frozen Morphology on Nanometer Scale in
Binary Blends: Computer Simulation of Microphase
Separation.
- P58 V.I.Loizinsky, A.L.Zubov, E.I.Titova
PVA-Cryogels Macro- and Microheterogeneities Induced by
Fillers of Various Porosity.
- P59 Yu.S.Yablokov, A.I.Prokofev, A.A.Litmanovich, I.M.Papisov
Polymer-Metal Nano-Composites Obtained by Matrix Red-Ox
Polyreactions.
- P60 M.Klapper, G.Gans, R.Gereke, L.Wang, S.Valiyaveetil,
U.Hoffmann, A.Parthiban, A.LeGuen, K. Mullen
Structural Organisation of Polymer Lattice Using Hydrogen
Bonds and Alkyl Chain Crystallisation.
- P61 A.V.Lyulin, J.P.Ryckaert, M.Destree
Influence of the Solvent on Helical Structure of Isotactic
Polypropylen. Molecular Dynamics Simulation.
- P62 G.I.Timofeeva, I.I.Ponomarev, R.Mercier
Associative Behavior of Water Soluble Rigid-Rod Sulfonated
Polynaftoyleneimide.
- P63 V.Kazakova, V.Myakushev, A.Muzafarov
Hyperbranched Ethylsilicate-Inorganic Polymer of Dendritic
Structure
- P64 E.V.Getmanova, O.B.Gorbacevich, T.B.Chenskaya,
A.M.Muzafarov
Polycarbosilanes of Dendritic Structure. Synthetical
Approach of Hydrophilisation.

- P65 V.A.Sergeev, N.I.Bekasova, M.A.Surikiva, E.A.Baryshnikova,
N.M.Mishina
Halatopolymers of m-Carboranedicarboxylic acid for
Introduction of Metals in the Free Fine-Grained State into
Polymers.
- P66 V.A.Sergeev, L.I.Vdovina, A.I.Vasilkov, Yu.V.Smetannikov
Synthesis of Metal-Containing Oligomers and Polymers on
the Basis of Oligo- and Polyarylenes and Atomic Metals.
- P67 A.I.Konstantinov, T.I.Shabatina, G.B.Sergeev
The Phase Transition Temperatures of the Thin Liquid
Crystalline Films Capsulated in Poly-para-xylylene.
- P68 I.I.Tverdokhlebova, W.K.Schitikov, N.N.Kudryavtseva,
V.A.Sergeev
Nano-Architecture of Polymethylenphenoles. Synthesis and
Properties.
- P69 L.V.Dubrovina, S.S.A.Pavlova, N.Ju.Kobak, E.A.Gladkova
Anomalous Micellization of Multiblock Copolymer in
Selective Solvent.
- P70 O.I.Shchegolikhina, I.V.Blagodatskikh, T.A.Larina,
A.A.Zhdanov
Novel Organosiloxane Polymer Systems with Strongly
Associating Groups.
- P71 V.G.Krasovskii, N.A.Sasovskii, A.M.Muzafarov
Fluorescently Labeled Organosilicon Dendrimers and
Quantitative Estimation of Filling Density of Dendritic
Structures.
- P72 V.A.Vasnev, G.D.Markova, S.V.Vinogradova, V.Yu.Voytekunas
Macromolecular Design in Polycondensation.

P73 S.Forster, E.Wenz, M.Zisenis, M.Antonietti
Micellization of Block Copolymers in the Super Strong
Segregation Regime

P74 P.Haaland, H.Jiang
On Texture and Laplacian Growth by Gas Phase Cationic
Polymerization

LECTURE SESSION 8

(Chairman - K.Yoshikawa)

17.00 - 19.00

Oral lectures:

OL28 K.N.Bakeev, S.A.Chugunov, T.A.Larina, W.J.MacKnight,
17.00 A.B.Zezin, V.A.Kabanov
Ionomer-Surfactant Self-Assembly in Low-Polarity Solvents

OL29 D.Hourdet, F.L'Alloret, R.Audebert
17.20 Thermoassociation of Polyacrylate Derivatives in Water

OL30 S.I.Klenin, I.A.Baranovskaya, V.O.Aseyev
17.40 The Nonlinear Change in Conformation of Polyelectrolyte
Macromolecules in Saltless Water-Organic Solvent

OL31 R.Borsali
18.00 Dynamic Scattering from Complex Polymeric Systems

OL32 G.Li
18.20 Interactions Between Polymer Molecules and Lyotropic
Liquid Crystal Phases at Concentrated Surfactant
Solutions

OL33 A.E.Rowan, P.Aarts, A.Schenning, B.de Bruin, R.J.M.Nolte
18.40 The Development of Polymeric Paraquat Host-Guest Complexes

TUESDAY, 23 MAY

LECTURE SESSION 9

(Chairman - M.Antonietti)

15.30 - 17.30

Oral lectures:

- OL34 V.A.Davankov, M.P.Tsyurupa, M.M.Ilyin, G.I.Timofeeva
15.30 Intramolecularly-Hypercrosslinked Polystyrene - A Novel
Macromolecular Nano-Species
- OL35 K.Dusek
15.50 Nanoinhomogeneities in Polymer Networks
- OL36 Yu.Ya.Gotlib, A.Gurtovenko
16.10 Theory of Dielectric Relaxation in Polymer Networks with
Different Structure
- OL37 H.Frisch, Y.Xue, S.Maaref
16.30 Inorganic/Organic Composite (Interpenetrating) Polymer
Networks Based on Zeolite 13X and Polystyrene and
Polyethylacrylate
- OL38 L.Z.Rogovina, V.G.Vasil'ev
16.50 Comparison of Association Processes in Physical Gels and
in Polymers with Small Number of Stickers
- OL39 Y.Rabin, S.V.Panyukov
17.10 Statistical Physics of Polymer Gels

LECTURE SESSION 10

(Chairman - J.Blackwell)

18.00 - 19.40

Oral lectures:

- OL40 T.Nose
18.00 Interfacial Tension of a Demixed A/B Polymer Blend with
A-B Diblock Copolymer near the Critical Point

- OL41 R.J.Spontak, S.D.Smith, M.M.Satkowski, R.L.Jones, A.Ashraf
18.20 Phase Behavior of, and Intramicrodomain Block Segregation
in Perfectly-Alternating (AB)_n Multiblock Copolymers
- OL42 I.Noda, Y.Matsushita
18.40 Morphology and Domain Size of a Model Graft Copolymers
- OL43 G.Floudas, G.Fytas, S.Pispas, N.Hadjichristidis, T.Pakula,
19.00 A.R.Khokhlov
Statics and Dynamics of ω -Functionalized Block Copolymers
of Styrene and Isoprene
- OL44 J.Laurer, R.J.Spontak, S.D.Smith, J.Samseth, A.Ashraf
19.20 Effect of Monomer Sequencing on the Equilibrium Phase
Behavior of Block Copolymers and Their Blends

WEDNESDAY, 24 MAY

LECTURE SESSION 11

(Chairman - T.M.Birshtein)

14.00 - 16.00

Oral lectures:

- OL45 A.N.Semenov, J.-F.Joanny
14.00 Adsorption of Linear Homopolymers: Equilibrium and
Dynamics
- OL46 A.N.Ozerin, A.V.Rebrov, N.F.Bakeev
14.20 The Structure of the Interface Boundaries in Polymer
Systems as Revealed by Small-Angle X-Ray Scattering
- OL47 K.Craemer, A.Wawkuszewski, H.-J.Cantow, S.N.Magonov
14.40 Scanning Force Microscopy in Surface Analysis of Polymers
- OL48 L.A.Feigin
15.00 X-ray and Neutron Reflectivity Studies of Langmuir-
Blodgett Films Containing Polymers

- OL49 Y.M.Lvov, K.Ariga, I.Ichinose, T.Kunitake
15.20 Molecular Film Superlattices Organized from Opposite
 Charged Polyions (Biological, Organic and Inorganic) by
 Means of Alternate Adsorption
- OL50 R.G.Winkler, P.Reineker, R.H.Schmid, R.Hentschke
15.40 Self-Organization of Liquids at Interfaces and in Thin
 Films: a Molecular Dynamics Simulation Study

LECTURE SESSION 12

(Chairman - H.-J.Cantow)

16.30 - 18.00

Oral lectures:

- OL51 S.Yu.Zaitsev, V.P.Vereschetin, E.A.Baryshnikova,
16.30 O.S.Novikova, V.P.Zubov
 Polymerization and Molecular Recognition in the Monolayers
 of Synthetic and Natural Compounds
- OL52 V.V.Klechkovskaya
16.50 Electron Diffraction Study of the Structure of Different
 Kinds of Langmuir-Blodgett Films
- OL53 J.Baschnagel, K.Binder
17.10 On the Influence of Hard Walls on Structural Properties in
 Polymer Glass Simulation
- OL54 J.Meyer
17.30 On the Chemistry of Metal-Rich Niobium Halides

THURSDAY, 25 MAY

LECTURE SESSION 13

(Chairman - A.B.Zezin)

09.00 - 11.00

- PL8 Plenary lecture
09.00 V.Percec
 Towards Tobacco Mosaic Virus-Like Self-Assembled
 Supramolecular Architectures

Oral lectures:

- OL55 V.P.Zubov, V.V.Egorov, S.Yu.Zaitsev
09.40 Polymer Biomimetic Systems: Design, Properties and Applications
- OL56 K.Yoshikawa
10.00 Kinetics of Collapse and Decollapse of a Single Double-Stranded DNA Chain
- OL57 K.V.Shaitan
10.20 The Topological Structure of Hypersurfaces of Conformational Energy Levels and Physical Mechanisms of Internal Proteins Mobility
- OL58 B.Duplantier, G.Jannink, J.-L.Sikoray
10.40 Dynamical Coupling Between DNA and Topoisomerase

LECTURE SESSION 14
11.30 - 13.30

(Chairman - R.Audebert)

Oral lectures:

- OL59 N.Kumazawa, Y.S.Mel'nikova, K.Yoshikawa
11.30 Novel Method to From Giant Liposome Entrapping DNA
- OL60 V.A.Izumrudov, M.Zhiryakova, S.I.Kargov
11.50 Competitive Reactions in Solutions of DNA-Containing Polyelectrolyte Complexes
- OL61 V.K.Fedyanin
12.10 Non-linear Excitations in Alpha-Helix and B-Form of DNA - Molecule
- OL62 I.M.Papisov
12.30 Composites Obtained via Matrix and Pseudo-Matrix Processes (Polymerization and New Phase Formation)

OL63 N.K.Balabayev, O.V.Gendelman, L.I.Manevitch, M.A.Mazo
12.50 Essentially Nonlinear Effects in Statics and Dynamics of
Polyethylene Crystal: Analytical Study and Numerical
Simulation

OL64 G.Alleggra, S.V.Meille
13.10 Chiral Crystallization of Polymer Chains

LECTURE SESSION 15

(Chairman - K.Dusek)

15.00 - 16.20

Oral lectures:

OL65 N.K.Balabaev, O.V.Gendelman, L.I.Manevich, M.A.Mazo
15.00 Self-Assembly of Domain Wall of Molecular Twist Defects
in Polyethylene Crystal

OL66 H.A.Schneider, M.Bolsinger, D.Brizzolara, S.Kurz
15.20 Side-Chain Crystallization of Amorphous Polymers due to
Self-Assembling Induced by CT-Interaction

OL67 V.A.Marikhin, L.P.Myasnikova
15.40 The Singularities of Interfacial Regions in Semi-
Crystalline Polymers

OL68 S.Piccarolo, G.Hitchcock, V.Brucato
16.00 An Experiment to Study Polymer Structure Development under
Pressure and at High Cooling Rates.

LECTURE SESSION 16

(Chairman - N.A.Plate)

16.50 - 18.00

Oral lectures:

OL69 V.G.Oshmyan, S.A.Timan
16.50 Simulation of Elastic and Superelastic Behavior of
Disordered Continua

OL70 B.L.Schuermann
17.10 Computer Simulations on Novolak-Phenol Formaldehyde Resin

OL71 O.V.Gendelman, L.I.Manevitch
17.30 On the Mechanism of Plastic Deformation of Simple and
Polymeric Glasses

17.50 CLOSING OF THE CONFERENCE

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Abstracts

HIERARCHICAL STRUCTURES IN NANO-LAYERED POLYMERIC SYSTEMS

E.Bacr

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SHAPE PERSISTENT MACROMOLECULES AS BUILDING UNITS OF COMPLEX SUPRAMOLECULAR ARCHITECTURES

GERHARD WEGNER

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Supramolecular structures of rigid and thus shape-persistent rods embedded in a continuous matrix of flexible chain segments, which are attached as side chains to the shape persistent backbone elements, are the central object of this contribution. Some of the polymers built along this principle can be processed by solution casting or even melt extrusion. The more interesting materials concerning aspects of supramolecular chemistry and molecular devices are obtained by Langmuir-Blodgett (LB)-technique. Monodomain textures of macroscopic dimension are readily prepared by the latter process. Flow in the monolayer film at the air-water interface in the course of the monolayer transfer to solid substrates orients the backbones of the "hairy-rod macromolecules" (HRM) towards the substrate, that is into the dipping direction. Thus, the orientation of the polymer chains in consecutive layers is adjusted by control of the rheological processes in the Langmuir layer and by the dipping direction.

The alkyl-side-chains of the HRM are in general designed to be non-crystallizing. This prevents formation of an inhomogeneous polycrystalline domain structure in the LB-layers. The multilayers of HRM are thus described as molecularly reinforced liquids. The fluid-like character enables the incorporation of guest molecules or covalently attached functional groups without destroying the regularity and homogeneity of the layered assemblies. The chemistry of the backbone elements of the HRM has to conform to shape persistence as a structural principle. Structures based on phthalocyaninatopolysiloxanes (PCPS), alpha-helical polyglutamates (PG), polysilanes (PSI), poly-p-phenylenes (PPP) and cellulose alkylethers (IPC) have been thoroughly investigated. In addition, periodic superstructures based on alternating layers of different such HRMs and structures in which one type of HRM was embedded as a guest within individual monolayers of another HRM have been made.

HRM which contain crosslinkable side chains have also been prepared. Processed into multilayered assemblies these can be crosslinked resulting in a network which is unidirectionally reinforced by the HRM. Such novel networks have been tested as size exclusive and osmotic membranes *vis. polymers*.

It will be demonstrated that HRM augment the toolbox of supramolecular architects substantially and are most useful in the construction of complex architectures to be used in planar optics, field effect devices, orientation layers in LC-devices and for tunneling diodes. Recent reviews are

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2. K. Mathauer et al., *Macromolecules* (1995) in press
3. D. Neher, *Adv. Materials* (1995) in press

COIL-GLOBULE TRANSITION: SELF-ASSEMBLY OF A SINGLE POLYMER CHAIN

by

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and

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Laser light scattering experiments on the self-assembly of a single homopolymer chain from the coil state to the globular states is discussed. The collapse transition for polystyrene in cyclohexane can be achieved kinetically by crossing the coexistence curve from the one-phase region to the two-phase region at finite concentrations, while that for poly(*n*-isopropylacrylamide) in water can be achieved under equilibrium conditions which permit experimental determinations of not only the hydrodynamic radius of the collapsed globule, but also its radius of gyration. It is noted that the collapsed globule of either system still contains large amounts of solvent.

SELF-ASSEMBLING WITH FORMATION OF MESOMORPHIC POLYMER STRUCTURES IN NON-MESOGENIC SPECIES.

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Classical liquid crystals are well known to be designed on the bases of either mesogene-containing organic molecules or molecules having amphiphilic structure. The number of LC compounds was strongly broadened in the last few years using the noncovalent binding of complementary molecules. It permits to design typical mesogenic fragments, to regulate their shape and length and to create new low molecular mass and polymer liquid crystals.

The aspect of this field which remains still unknown is whether this approach is useful to create organized ordered systems based on amphiphilic molecules. To fill in this gap we suggested a route to build amphiphilic structures based on nonamphiphilic components which contain linear polyacids (or dicarboxylic acids) and tertiary amines (or tertiary amine hydrochlorides) having non-mesogenic or mesogenic-like molecular structure.

The formation of hydrogen bond complexes with the partial charge transfer proved by FT-IR measurements and other technique results in the change of lipophilic-lipophobic balance in the system due to complex formation and this induces microsegregation processes. This behavior can be responsible for the lamellar-like supramolecular order which results from the arrangement of amine residues attached to acid molecules via H-bonds. Acid microphases perform as an "aqueous" interlayer in lyotropic liquid crystals and stabilize the ordered structure both in bulk complexes and LB films. Such complexes could be considered as a particular group of liquid crystals which is displaced at the boundary between the thermotropic and lyotropic systems

Acknowledgements

This research has been supported partially by grants from the International Science Foundation (N M000R) and Russian Foundation of Fundamental Research (N 94-03-09535).

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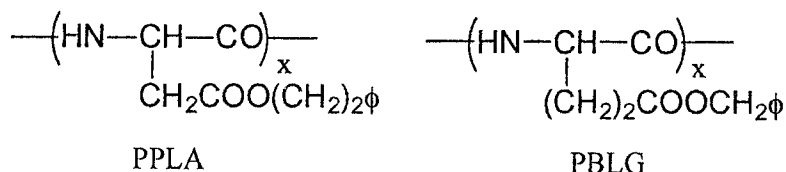
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Conformational Transitions and Incidental Reorganization of Mesophase Structures Peculiar to Polyaspartates – A Highly Versatile System Designed by Nature

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Polypeptides such as poly(β -phenethyl L-aspartate) (PPLA) and poly(γ -benzyl L-glutamate) (PBLG) are man-made polymers having the poly-L- α -aminoacid sequence along the backbone with an ester group in the side chain. The essential parts of these polymers are originally born in nature. PPLA and PBLG are mutually isomeric in their chemical structures:



I.e., PBLG can be converted into PPLA by interchanging γ -CH₂ with the ester group in the side chain. Both PPLA and PBLG form an α -helix in various organic solvents, which by addition of denaturant acid, transforms to a random-coil. Yet the physical properties of these two polymers are quite different. While the α -helical PBLG is known only in the right-handed form, PPLA can be either in the right- or left-handed arrangement depending on the solvent or temperature. The latter behavior is widely known as a characteristic of the poly(aspartic acid ester)s.

Phase diagrams comprising a ternary components PBLG/EDC/DCA are known to form liquid crystals above certain concentration at room temperature. The liquid crystalline phase reaches high and low temperature isotropic region, respectively, on heating and cooling. The polymers are random-coil in the low temperature isotropic phase. Our recent investigation indicates that PPLA/CHCl₃/TFA could possibly exhibit as many as five phases. In addition to the three described above, the sense of the PPLA helix transforms in the order left \rightarrow right \rightarrow left within the liquid crystalline state. The transformation of r- to l-PPLA or vice versa inevitably induces the inversion of the screw sense of cholesteric mesophase. In this talk, I would like to emphasize an important role of the sidechain conformation flanking the α -helical backbone in these phase transitions.

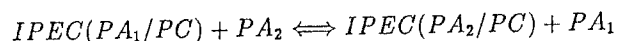
* In collaboration with Drs. H. Furuya and S. Okamoto, Department of Polymer Chemistry, Tokyo Institute of Technology.

MOLECULAR RECOGNITION PHENOMENA IN POLYELECTROLYTE SYSTEMS

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Polyanion/Polycation Recognition. It is known that cooperative coupling reactions between two oppositely charged polyelectrolytes in aqueous solution result in formation of interpolyelectrolyte complexes (IPECs). Such IPECs can be formed practically by any polyanion/polycation (PA/PC) pair. However, in the systems containing, for example, two chemically different PA (PA_1 and PA_2) PC has a choice to form either IPEC (PA_1/PC) or IPEC (PA_2/PC), or both. In other words in an equilibrated system the situation can be described by the position of equilibrium



The situation when equilibrium is completely shifted to the left or to the right means that in spite of universality of electrostatic attraction force PC strongly prefers one of the two PA, i.e. "recognizes" it. Such recognition phenomena are demonstrated and it is shown that the extent of recognition is determined by the chemical structure of interacting polyions, and can be effectively controlled by their lengths (DP), concentration of the low molecular salt and the nature of the counterions as well as by a small molecular vector group attached to the one of the polymer partners.

Polyion/Latex Recognition. The possibility of recognition and discrimination of relatively large charged supermolecular objects (latex species) by an oppositely charged targeted polyion is demonstrated. The suspension of protein - modified latex particles interacting with the high molecular mass linear polycations (poly-4-vinylpyridinium) conjugated with the specific protein (α -chymotrypsin) was used. The polycations are strongly adsorbed on the latex surface. Nevertheless, they are able to migrate between the latex species via occasional interparticle contacts. Finally the polycations carrying the specific protein are fixed on those latex particles which carry the complementary protein receptor (trypsin inhibitor from soybean). The presence of other proteins does not hinder such interaction. The obtained effect is considered to mimic a physico-chemical aspect of recognition of target cells by macromolecules combined with relatively small molecular vectors.

Metal Ion Recognition by Prearranged Polyelectrolyte Networks containing complexing groups is demonstrated. Prearrangement was achieved by interacting a linear polymer precursor with certain metal ions followed by a chemical cross-linking of the linear chains carrying complexed metal ions. Then the metal ions were removed. It is shown that such a prearranged sorbent absorbs much faster and bind much more of the corresponding metal ions than that of the same composition and degree of cross-linking but not prearranged.

MORPHOLOGICAL VERSATILITY IN THE SELF-ASSEMBLY OF BLOCK POLYELECTROLYTES IN AQUEOUS ENVIRONMENTS

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It is known that block copolymers in bulk self-assemble to give four well-defined morphologies; with changing composition, one sees spheres, rods, the ordered bicontinuous double-diamond (OBDD), lamellae, and the OBDD, rods and spheres of the opposite composition. These have been explored in considerable detail. Small molecule amphiphiles are also known to give three morphologies, i.e. spheres, rods and vesicles. Now, with the advent of ionic block copolymers and their precursors, some of these morphologies, among others, have also been shown to exist in solutions and on surfaces.

Highly asymmetric amphiphilic block copolymers with the hydrophobic segment as the major component are discussed first. It is shown that in polar solvents (e.g. water), using polymer chains of up to 90 cores can be prepared. These micelles can be described as "crew-cut". At ca 92 or lamellar at ca 96 of large spheres filled with reverse micelles but possessing a hydrophilic surface which makes them stable in aqueous solutions. Obviously, simple reverse micelles exist in non-aqueous solutions of the same polymers.

Very similar morphologies exist in two dimensions when similar amphiphilic polymer are deposited on water surfaces. Thus, depending on the exact composition, circular, ribbon-like and lamellar morphologies are seen which are the exact analogues of the three-dimensional micelles. Also, a foam-like morphology can be prepared which can be considered as the phase-inverted version of the circular micelles or the two-dimensional analog of the large sphere morphology in 3 dimensions.

When the spherical (3D) micelles in aqueous solution are deposited on a glass plate and dried, an exceptionally regular needle-like crack-pattern develops. The needles are highly birefringent and stable. These phenomena, just as the existence of stable 3 dimensional block copolymer micelles of non-spherical morphologies, are believed to be new.

TOWARDS TOBACCO MOSAIC VIRUS-LIKE SELF-ASSEMBLED SUPRAMOLECULAR ARCHITECTURES

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Viruses are most frequently self-assembled into rod-like and icosahedral shapes¹ and represent the best understood self-assembled natural systems. The classic example of rod-like virus is Tobacco Mosaic Virus (TMV).² Regardless of its shape (i.e., rod-like or icosahedral), a virus consists of a RNA or DNA chain coated with proteins of a well defined shape (*exo*-receptor and *exo*-recognition) which are ultimately responsible for the rod-like or icosahedral shape of the virus and for the well defined conformation adopted by the nucleic acid chain. In the case of TMV the tapered shape of the coating proteins generates the rod-like self-assembled supramolecular architecture. The interaction between the nucleic acid and protein (*endo*-recognition) is responsible for the stability, length and diameter of the rod. At the same time, the insertion of the nucleic acid into the center of the rod-like architecture induces its helical conformation. TMV can also self-assemble in the absence of RNA, but its length is not controllable under these conditions. We are investigating the self-assembly of various tapered (*exo*-receptor) groups into rod-like shapes.^{3,4} By analogy with the self-assembly of TMV we are capable to generate a cylindrical architecture with a well defined diameter in the presence and in the absence of synthetic polymer chains. This presentation will discuss the dependence between the shape and size of synthetic tapered groups and their ability to self-assemble into rod-like and other shapes via various *endo* recognition processes. The use of various polymer backbones which are either covalently or noncovalently bonded to these groups to provide this self-assembly process will also be discussed. The dependence between the structure of various chains and their ability to adopt, most probably, a helical configuration within the core of the rod will be considered as a new mechanism for the induction of chirality based on single chain helicity. Finally, the control of some properties of these rods via the chemical structure of their surface and their use as one, two and three dimensional ionic, electronic, etc. channels will be presented. Several other examples of synthetic systems generated by using Nature as a model will be described.

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KINETICS OF CONFORMATIONAL CHANGE OF POLYMERS - COIL - TO GLOBULE TRANSITION

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There is considerable interest in understanding the kinetics of conformational changes in polymers, heteropolymers and biopolymers. Different approaches, both experimental, computational and theoretical are currently being discussed in the literature. We discuss some of these.

In particular we discuss how the approaches of non-equilibrium Statistical Mechanics can be used to understand the homopolymer coil-to-globule kinetics, and the conformational changes of random co-polymers. We present the kinetic laws, and describe the underlying processes.

HOW TO DESIGN HETEROPOLYMER WITH A “SMART” SEQUENCE?

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In the case of proteins, the unique 3D fold, responsible for the particular functionality of the molecule, is determined by the sequence of monomer units. We suggest a procedure, which we call Imprinting, to control the monomer sequence of an artificial heteropolymer during its synthesis in order to obtain a heteropolymer with the protein-like capability of memorizing some unique spatial fold that allows certain functional properties, such as the specific molecular recognition of a given target molecule. To control the sequence, our procedure employs interactions between monomers; in other words, our method allows the monomers themselves to “design” the polymer. We show that the procedure leads to renaturable chains, because renaturation is governed by the same interactions between monomer units. We present both analytical and computational study of Imprinting, yielding the requirements on “chemistry” (the set of monomers chosen) and specific prescriptions for the experimental verification of this theory.

We stress several important advantages of Imprinting: (i) it does not employ any products of biological evolution, such as synthetic apparatus of the living cell; (ii) it is not restricted to the use of the amino acid chemistry of real proteins; (iii) from the theoretical perspective, neither the solution of the direct nor inverse protein folding problem is required. Indeed, we do not purport either to compute the 3D structure for a given 1D sequence (direct) or to compute the 1D sequence to fold to a given 3D structure (inverse); (iv) our approach also does not involve evolutionary time scales, and is supposed to work thermodynamically, as a sort of “evolution in a test tube.”

We examine also the role of possible differences between interactions governing the design and folding behavior (“misunderstandings” in the folding code), and the role of external field(s) applied on the design and/or folding stage.

As to theoretical perspective, we use the simple approach, similar to REM, thus avoiding difficulties of the replica field theory.

MACRO- AND MICROPHASE SEPARATION IN POLYMER SOLUTIONS
IN NEARLY CRITICAL LOW-MOLECULAR SOLVENTS

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Thermodynamic and static correlational characteristics of polymer systems contained in nearly critical low-molecular solutions are studied using an exact representation of the partition function of the systems under consideration as a two-field continual integral. Using the corresponding diagram technique we present a variational principle enabling to calculate both the effective free energy and correlation functions of the polymer solution under consideration explicitly. It is shown that all higher vertices of the corresponding effective hamiltonian increase when approaching critical point of the solvent, the two- and four-monomer effective interactions being corresponded to attraction and repulsion respectively. The interplay among these two competing factors can result in a solubility increasing or microphase separation (weak super-crystallization) depending on material constants describing the system under investigation. The corresponding phase diagrams are presented.

INTERNAL HYDRODYNAMICS OF POLYMER COILS OR SPHERICALLY
SYMMETRIC AGGREGATES IN DILUTE SOLUTIONS

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A new model for polymer dynamics is introduced. The model represents a polymer coil or stable aggregate as a solution of monomers in the force field $\vec{F} = \vec{F}_s + \vec{F}_e$, where $\vec{F}_s(\vec{r}) = -k_B T \text{grad}[\ln n_0(\vec{r})]$ is the entropic force, which tends to establish equilibrium local monomer number density $n_0(r)$, and \vec{F}_e is an external field. The dynamics of the model proposed are governed by well-known equations of liquid blend hydrodynamics in external fields. This model is alternative to the pearl-necklace and rigid porous sphere (RPS) models. It has an advantage of mathematical simplicity over the pearl-necklace model and is capable to take into account variations of coil local density as distinguished from the RPS model.

The hydrodynamic equations were solved for the cases of uniform and shear flows and the coil translation diffusion coefficient and the intrinsic viscosity were calculated for the equilibrium density in the form $n_0(\vec{r}) = [(3-\lambda)/4\pi] N R_s^{\lambda-3} r^{-\lambda} H(R_s - r)$, where N is the number of monomers in a coil, $H(x)$ is the step function and R_s is related to the radius of gyration R_G by the equation $(3-\lambda)R_s^2 = (5-\lambda)R_G^2$. Calculation were made also for the Gauss density distribution. The results were compared with those obtained using the RPS model. If our equations are solved within the extreme dilution approximation the both models give rather close results. The perspectives of the proposed model development are discussed.

X-RAY ANALYSES OF THE SUPRAMOLECULAR TUBULAR STRUCTURES FORMED BY A POLY(METHACRYLATE) WITH HIGHLY TAPERED SIDE GROUPS, by L. Blackwell, Y. K. Kwon, S. N. Chvalun, C. A. Danko, V. Percec and J. A. Heck, Case Western Reserve University, Cleveland, OH 44106-7202, USA

A poly(methacrylate) with highly tapered side chains: poly {2-[2-[2-(2-methacryloyloxyethoxy)ethoxy]ethoxy]ethyl-3,4,5-tris(p-dodecyloxy-benzoyloxy) benzoate}, has been shown to form an ordered hexagonal structure at room temperature, and to undergo transitions to a columnar hexagonal (ϕ_h) phase above $\sim 40^\circ\text{C}$ and to an isotropic phase above $\sim 100^\circ\text{C}$. In the ϕ_h phase the structure consists of cylinders of diameter 60.4\AA at 40°C , decreasing to 53.0\AA at 95°C , in which there is little internal order other than limited stacking correlations for the side chains. In the ordered hexagonal state at room temperature, the cylinders have an ordered internal structure with an axial repeat of 5.03\AA . Based on the observed density, this repeat would contain 8 monomer units within a cylinder of diameter 59.8\AA (at 21.6°C). Several possible 8-fold models for the stacked side chains have been considered, and the simulated scattering patterns for an 8_1 helical model are found to be in qualitative agreement with the observed X-ray data. The changes in cylinder diameter with temperature in the ϕ_h phase correlate very well with the striking dimensional changes observed for the oriented fibers between 40°C and 95°C : we see a 14% decrease in width and a 28% increase in length, suggesting a progressive rearrangement of the supramolecular organization. Parallel investigations of the structure of the unpolymerized monomer precursor also show the existence of supramolecular assemblies forming ordered hexagonal and ϕ_h phases.

COMPUTER DESIGN, SYNTHESIS AND INVESTIGATION OF GRADIENT-MODULUS POLYMERS

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The preparation of the gradient-modulus polymer materials is based on a general idea which allows wide variation of the mechanical, optical and other properties of a polymeric material to be accomplished with the same sample or article. The problem of producing of transparent polymeric materials having the elastic modulus typical of polymers in the transition zone from glassy to rubbery state but at the same time possessing elastic rather than viscoelastic properties has been solved. The solving this problem is, on theoretical grounds, that the structure of the networks possessing given properties comprises rigid bulky junction points and very flexible and short networks chains linking them. The role a crosslinked point is played by a trifunctional isocyanurate ring with adjacent benzene rings, while the role of network fragments is played by very short organosilicon or tetramethyleneoxide chains. As a result the gradient-modulus polymeric materials have been prepared, which show a continuous transition, within the same sample, from rubber to plastic without any junctions, joints, etc. These materials are elastic and have a modulus ranging from 3 to 3000 MPa. The properties of the materials were calculated before their synthesis. It was shown that a prerequisite of such materials is the occurrence of microphase separation. The compositions of microphases have been calculated.

Biodegradable stereocomplexes and block copolymers - Strategies for novel interfaces

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Poly-L-Lactide (PLLA) and Poly-D-Lactide (PDLA) crystallize into a stereocomplex exhibiting a 50° higher melting point than both the PLLA and the PDLA crystals. The unit cell of the racemic crystal has the dimensions $a = 9.16 \text{ \AA}$, $b = 9.16 \text{ \AA}$, $c = 8.7 \text{ \AA}$, $\alpha = 109.2^\circ$, $\beta = 109.2^\circ$, $\gamma = 109.8^\circ$. Two 3_1 -helices (β -form) of PLLA and PDLA are packed with parallel orientation. The molecular simulation of the complex using the Dreiding-Force-Field fairly agrees with the experimental cell data. Van der Waals contacts indicate that stabilising interactions between opposite methin protons and carbonyl groups are formed, causing the high stability of the complex.

To optimize the stereocomplex formation we investigated the growth of lamellar stereocomplex and component crystals from dilute solutions. By WAXS and by molecular simulation of the PLLA crystals two crystallographically similar cell types were verified, a hexagonal unit cell, with four 3_1 -helices in the cell, and a orthorhombic unit cell containing two 3_1 -helices.

Melt spun PLLA fibres form a orthorhombic cell containing two 10_3 -helices (α -form). In fibres from semidilute solutions with high molecular weight ($M_v = 5 \cdot 10^5 \text{ g/mol}$) and high draw ratios the β -structure appears. The difference of spacings and of the type of helices in the fibre and in solution grown crystals is consistent with the different specimen morphologies: Stereocomplex formation in solution and in spun fibres strongly differs.

In solution *pure* racemic stereocomplex is only formed using molecular weights below $M_v = 5 \cdot 10^3 \text{ g/mol}$. This fact supports the supposition that the stereocomplex is characterized preferentially by side-by-side adjacent entry of the PLLA and the PDLA loops. Applying higher molecular weights separate crystallisation of the components predominates.

Due to decreased chain mobility stereocomplex fibres contain racemic *and* component crystals. In fibres the stereocomplex formation depends on molecular weight and draw-ratio, which influences the portion of the 3_1 helices.

Polylactides and similar type biodegradable polyesters give the chance to prepare block copolymers by thermal esterification of components, which are properly end-functionalized. Combining those copolymers with stereocomplexes offers strategies to realize novel interfaces and supramolecular architectures, consequently. Those systems can combine the unique properties of stereocomplexes with the capability of triblock copolymers to perform two functions in parallel: To interact with the surface of the stereoblock crystals *and* to bridge them with an elastic middle block, i. e.

A CONTROL OF PRIMARY STRUCTURE IN THE PRODUCTS OF MACROMOLECULAR REACTIONS

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Properties of any tailor-made polymer material are determined in fact by a primary structure (PS) of macromolecules. The latter in the case of the product of macromolecular reaction (MR) is characterized by a distribution of reacted and unreacted units (DU) along the chain.

The theory of MR let analyze an influence of various factors on a PS of the forming macromolecules.

Previously MR of quasi-isolated macromolecules in diluted solutions have been considered. In such systems PS is determined by a competition between external reagent and intrachain interaction of reacted and unreacted units, first by the effect of neighboring units. Varying experimental conditions, it is possible to synthesize macromolecules with pure random (Bernoulli) DU as well as ones with a tendency either to block formation or to alternation.

In this paper we present new results related mainly to MR in a polymer bulk state, where the interchain interactions play a significant role.

In a melt, interchain effect shifts DU in the forming chain to Bernoulli one for both accelerating and retarding action of reacted units.

In a glass, a topochemical mechanism of the MR is likely; for intermediate conversion degrees the reaction system represents a blend of the initial polymer and the final product, the components being very intimately mixed (in some cases it is difficult to prepare such an intimate blend in a different way).

For MR in a polymer blend consisting of reacting and non-reacting but influencing the reactivity components, not only chemical factors but also interdiffusion affect a PS of the reacting macromolecules. Due to diffusion movements of two kinds, DU in the product chain declines from that of the product for the same MR in a melt of pure initial polymer.

Some new results related to conformational effects for MR in solutions have been also obtained recently. In particular, should an accelerating action of remote reacted units is commensurable with that of nearest neighbors, such a conformational effect enlarges the formation of alternating sequences of units.

Thus on the basis of modern achievements of the theory related to a wide set of reaction systems it is possible to choose optimal conditions for the preparation of tailor-made macromolecules.

Nanodispersed Metal and Metal Oxides Particles in Polymeric Matrices from Polyacrylonitrile Precursors

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The growing interest to metal colloids dispersed in polymeric matrices derives from the fact of their unique catalytic, ferromagnetic and non-linear properties. Nucleation and growth processes in solid polymeric matrices depend on many parameters including the type of a polymeric matrix, possibility of complex formation, conditions of colloid preparation and others. In this presentation we consider two approaches to the colloid formation of metals and metal oxides in the polyacrylonitrile (PAN) and its copolymer (1.5 wt % of itaconic acid) (PAN-I). Since such polymers contain nitrile groups capable to complex formation, metal particles might form both from organometallic polymers prepared via complexation of organometallic compounds with PAN with following decomposition of complexes and through blending an organometallic compound with polymers, although in this case miscibility between the two would be a paramount concern. Whereas PAN produces polycyclic structures with conjugated double bonds under thermolysis at 200-300°C, thermal decomposition of organometallic complexes is accompanied by reactions in a polymeric matrix.

We have studied the thermal decomposition of W, Mo and Cr carbonyl complexes with PAN, prepared by the interaction of PAN nitrile groups with VI B group metal hexacarbonyls. The thermolysis under air leads to a formation of metal oxides' particles which by X-ray fluorescence (XRF) analysis are evenly distributed in polymer film. For the Cr-containing PAN, the presence of dispersed Cr_2O_3 with a size less than 3 nm was estimated by ESR. The presence of metal oxides' colloids in thermolized PAN influences the conductivity of polymer films, in so doing MoO_3 and Cr_2O_3 increase the conductivity of thermolized films on 5-6 and 7-9 orders of value, respectively.

Co-containing polymers were prepared by mixing $\text{Co}_2(\text{CO})_8$ with PAN-I in DMF. It was found that $\text{Co}_2(\text{CO})_8$ interacts with DMF giving salt $[\text{Co}(\text{DMF})_6]^{2+}[\text{Co}(\text{CO})_4]^{-2}$. PAN-I appears to be compatible with $[\text{Co}(\text{DMF})_6]^{2+}[\text{Co}(\text{CO})_4]^{-2}$ until the Co content in the blends reaches 8 wt.%, as transparent pink films are formed. The colloid particle size was estimated by ferromagnetic resonance (FMR) and SAXS. It was established that the presence of Co compound accelerates the thermolysis roughly tenfold. According to XRF measurements, polymer films derived from PAN-I after thermolysis contain the Co particles uniformly distributed in polymer matrix. By FMR and SAXS, colloid size depends on thermolysis conditions and loading the Co complex and varies from 1 to 10 nm.

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NANOSIZE METAL CLUSTERS IN POLYMER SYSTEMS

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Methods of synthesis of polymer materials with nanosize metal clusters are currently of great importance from fundamental and applied viewpoints. New synthetic methods based on low temperature techniques have been developed in our laboratory. The main goal of these studies is to achieve the uniform distribution of particles with sizes less than 10 nm in polymer systems.

The cross-linked poly-acrylamide gel (PAG) was used as a matrix for (i) in situ synthesis and (ii) stabilization of silver nanoclusters.

(i) In situ synthesis of Ag-PAG was carried out in reverse micelles of AOT in nonane. Photoreduction of Ag^+ -ions and photopolymerization of acrylamide (AA) and N,N-methylene-bis-acrylamide (MBAA) were induced by the light of 250W Hg-lamp. According to TEM (Transmission Electron Microscopy) and UV-Vis-spectroscopy data the size of Ag-particles in stable Ag-PAG nonane dispersion is in the range of 2-15 nm depending on the selected ratio $[\text{H}_2\text{O}]/[\text{AOT}]$.

(ii) Silver nanoclusters produced as an organodispersion in acetone via a cryochemical route were trans-solvated into water dispersion by Triton X-100 and then was taken as a base for polymerization mixture (AA, MBAA and azo-bis-(isobutyronitrile)). Photopolymerization results in the transparent Ag-PAG with uniformly distributed Ag-particles of 15-20 nm size according to TEM.

The codeposition of metal (Ag, Pb, Zn, Cd) vapors with reactive monomer-p-xylylene at surfaces cooled by liquid nitrogen in vacuum with following heating from 80 K to 110-150 K results in the polymerization of p-xylylene and aggregation of metal atoms. As a result, poly-p-xylylene films containing metal clusters are obtained at room temperatures. According to TEM data the size of globular lead particles is in the range of 3-8 nm and independent on the lead content for 0,1-6,5 weight %. Zn and Cd particles of the same size appear to form more higher aggregates in poly-p-xylylene films. The IR data at 80 K indicated weak low temperature interaction of metal atoms and small clusters with p-xylylene which could be the reason for a rather uniform distribution of nanosize metal particles in poly-p-xylylene matrix at room temperature.

Cryochemical methods are perspective for synthesis the new polymer materials with nanosize metal clusters. Poly-p-xylylene films with metal clusters (resistance in the range of 10^{14} - 10^{16} ohm/cm²) was shown to exhibit some catalytic and sensor activity. Optical and electric properties of Ag-PAG are under way.

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SELFORDERING IN CYCLOLINEAR POLYORGANOSILOXANES

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It is well established now that flexible linear semiorganic polymers such as polydiorganosiloxanes, polydiorganosilanes and various polyphosphazenes are able to selfordering with the formation of thermotropic columnar mesophases despite of absence of any classical mesogens in their molecular structure. The most important molecular parameter controlling the mesophase behaviour and the temperature interval of the mesophase stability in the linear macromolecules is the nature and length of the side organic substituents. On the other hand, in our studies [1-3] we have demonstrated that some flexible oligo- and polyorganosiloxanes with cyclolinear structure of the backbone, which also do not contain classical rigid rodlike or disclike mesogens, can form thermodynamically stable ordered thermotropic mesophases, which in many respects are closely related to columnar and smectic mesophases. In contrast to linear semiorganic macromolecules in the cyclolinear systems there are a number of additional molecular parameters such as the ratio of linear and silsesquioxane fragments within the macromolecules, spatial arrangement of the substituents within the organosilsesquioxane fragments, which can be used to influence on the mesophase behaviour. Moreover, although most of the cyclolinear macromolecules are rather flexible their rigidity can be gradually regulated due to increasing the number of bulky substituents such as phenyl. In this presentation the selfordering of cyclolinear oligo- and polyorganosiloxanes is considered with particular emphasis on the temperature stability of the mesophases as a function of molecular structure, molecular weight, the nature of substituents. The character of packing of macromolecules in the mesomorphic state is considered. The formation of the self-ordered mono- and multilayers is also discussed.

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ELECTROOPTICAL PROPERTIES OF NOVEL FERROELECTRIC LIQUID CRYSTAL POLYMERS

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In 1988 electrooptical switching in ferroelectric LC polymers has been reported for the first time¹⁻³). FLC polymers are expected to find application a) in flexible displays using ferroelectric, antiferroelectric, electroclinic or deformed helix mode electrooptical switching b) in non linear optics c) in piezoelectric elements and pyroelectric detectors.

This presentation deals with new FLC polymers of the polyacrylate, polysiloxane and polyvinylether type, which bear high polarization side groups with one and two centers of chirality.

Besides short bistable ferroelectric switching (200-400 μ sec; 10 V_{rms}(μ m) an even shorter electroclinic switching process will be discussed. Some representatives exhibit three state switching (antiferroelectric behaviour).

Variation of the spacer length results in a drastic change in the values of spontaneous polarization. Inclusion of chiral centers in the spacer resulted in a FLC-polymer that exhibits a sign reversal for the spontaneous polarization in the S_C* phase. Variation of the molecular weight revealed up to three subphases in the S_C* region.

"Diluting" a FLC-polymer by copolymerization with a non mesogenic comonomer resulted in a shift of the S_C* phase near to room temperature and in fast switching. FLC polymers containing fluorescent dyes were developed, which show broad S_C* phases and high values of spontaneous polarization. They are suitable for fluorescent devices exhibiting a large viewing angle.

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INTERFACE EFFECTS IN NEMATIC LIQUID-CRYSTALLINE STRUCTURES OF POLYMER SOLUTIONS

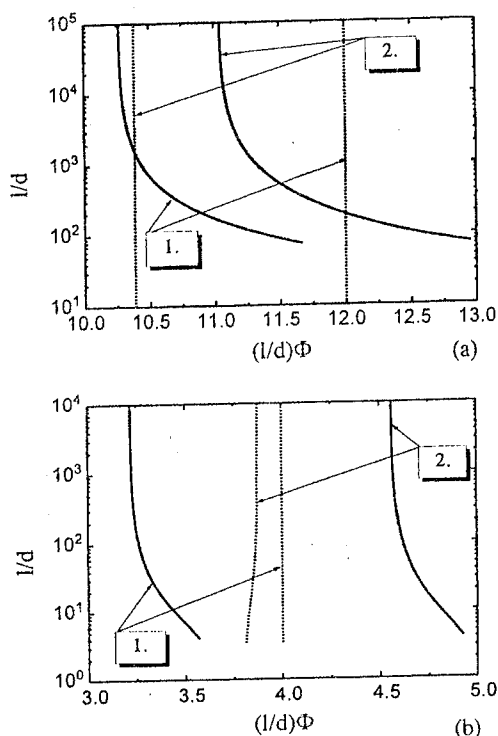
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A solution of the long semirigid linear macromolecules is considered under the condition $L \gg l \gg d$, where L , l and d stand for the polymer contour length, the effective segment length and the effective diameter respectively. The liquid-crystalline nematic ordering in the solution is analyzed theoretically using Onsager's type approach. The orientational entropy is calculated in the frameworks of Lifshits' approach, successfully developed for this system for the first time by Khokhlov and Semenov.

For homogeneous liquid-crystalline phase in the third virial approximation for intersegment steric interaction the orientation distribution function, the free energy density, the isotropic-nematic coexistence and the spinodal conditions have been computed numerically for two types of polymer flexibility mechanism: persistent chains and chains of freely joint segments. The applicability region for the asymptotically exact second virial approximation was analyzed. The calculated coexistence curves are shown in the Figure by the solid lines and the spinodal curves - by the dashed lines (part "a" corresponds to the persistent chains and part "b" - to the freely joint ones). Here the isotropic-side characteristics mark by 1 and the nematic-side ones mark by 2, Φ is the volume fraction of the polymer.

We considered the general type equations, describing concentration and orientation segment distribution for the semirigid persistent polymer chain in surfaces and interface boundaries of any shape and orientation. These equations for the case of perpendicularity of the nematic director axis and the plane interface boundary between the real coexisting nematic and isotropic phases were solved numerically. The results demonstrate a specific combination of the usual liquid-crystalline ordering and the characteristic surface ordering of non-liquid-crystalline nature, which is connected with the chain bending for its returning to the phase with higher concentration. The coordinate-dependencies of the polymer concentration and of the order-parameter have a smooth two-steps form in this region.



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Amorphous-LC-Blockcopolymers. Synthesis, Morphology and Phase Behaviour

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Based on anionic synthesis of poly(styrene-block-1,2-butadiene) and subsequent polymeranalogous conversion of the 1,2-butadiene units amorphous-liquidcrystalline diblock and triblockcopolymers were prepared. The morpholgy of the diblockcopolymers is of lamellar type with LC microdomains having smectic or nematic phases. The lamellar order, LC order and phase transitions were investigated by small-angle X-ray scattering and ^2H NMR spectroscopy in dependence on molecular weight and the nature of the liquid crystalline phase. Beside diblockcopolymers first results on the morphology and properties of a new type of material, thermoplastic liquid crystalline elastomers, are reported.

LIQUID CRYSTALLINE POLYMERS IN NEMATIC SOLVENTS: INTERFACIAL PROPERTIES

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Solutions of main chain liquid crystalline polymers (LCP) in nematic solvents exhibit novel interfacial behaviour. This is due to the coupling between the chain trajectory and the molecular field due to the nematic order. As a result, the LPCs are anisotropic, ellipsoidal objects. Furthermore, the anisotropic LCP can be oriented in space by aligning the nematic solvent. In particular, the nematic solvent can be aligned by surfaces imposing homogenous or homeotropic anchoring. Because of the combined effect of these ingredients, tilt becomes an option for LCP at interfaces. In a number of situations the onset of a tilt is associated with a second order phase transition. This behaviour is expected from free chains subject to confinement, from terminally anchored chains and from uniformly adsorbed ones. When this effect is combined with the Frederiks transition it allows for an arbitrary lowering of the critical potential. Similar considerations suggest the design of "smart materials" based on ABA triblock copolymers with a main chain LCP. Nematic mesogels based on these polymers are expected to exhibit a novel quasi piezoelectric behaviour, as well as mechano-optic effects.

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AGGREGATION AND GELATION OF POLY(OCTYL ISOCYANATE) IN NONPOLAR SOLVENTS

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Poly(alkyl isocyanates) are semiflexible polymers capable of forming liquid crystalline solutions. Dilute solutions of poly(alkyl isocyanates) are interesting due to the observed dependence of the persistence length of the polymer on the solvent polarity; the persistence length decreases with increasing polarity of the solvent.

Polyisocyanates form thermoreversible gels in certain nonpolar solvents. We have tried to understand the possible dependence of gelation on the stiffness of the polymer main chain. To enable the studies on the chain flexibility, poly(octyl isocyanate), POIC, and its spin labelled analogue were synthesised.

Paramagnetic nitroxide labels attached to POIC as side groups have been shown to detect solvent dependent changes in the flexibility of the polymer chain. Gelation of the solutions of the labelled POIC has a noticeable effect on the shape of their e.p.r. spectra. The spectra also indicate the strong tendency of the polymer to aggregate in several solvents.

POIC has been studied by e.p.r. spectroscopy and light scattering especially in two non polar hydrocarbon solvents. In the gel forming solutions, the temperature dependence of the chain flexibility has been observed to be stronger than in the solutions which do not form gels. The gelation is suggested to be a frozen-in phase separation of the stiff polymer.

SYNTHESIS OF MESOPOROUS POLYMERS IN LYOTROPIC LIQUID-CRYSTALLINE PHASES

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Lyotropic liquid crystals exhibit a rich structural polymorphism over nanometre length scales. This can be exploited for the synthesis of nano-structured inorganic and organic polymers, whose periodic architectures are casts of the mesophase structures.

Highly ordered, mesoporous silica with large specific surface area and an hexagonal array of uniformly sized channels was obtained via a sol-gel process occurring in a lyotropic liquid-crystalline phase[1]. The structure of the H_I phase[2], consisting of a nonionic surfactant and water, as well the progress of the silica formation was monitored by optical microscopy. The temporal evolution of oligomeric/polymeric molecular species was studied by ²H NMR spectroscopy.

This novel method is not restricted to homodisperse surfactants, but it can also be applied to polymeric amphiphiles. The materials obtained were characterised by transmission electron microscopy, X-ray diffraction and porosimetry. The results suggest that the synthesis of mesoporous molecular sieves can be applied to a large variety of surfactants and inorganic precursors, providing that the mixture, in which the polycondensation (solidification) of the inorganic precursor takes place, is liquid-crystalline. Further, it is possible to perform the photopolymerisation of a water-soluble, organic monomer within the aqueous region of the lyotropic liquid-crystalline phase. This indicates that mesophase-templated synthesis can also be applied to the production of nanostructured organic polymers.

This method of preparing nanostructured materials is of considerable interest because of the high degree of control that can be achieved over the nanostructure of the resulting polymer and the possibility of monitoring the progress of its formation.

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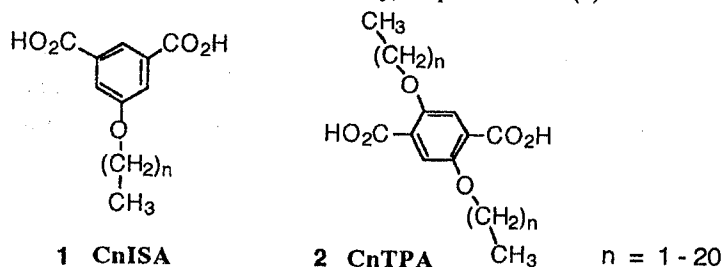
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HYDROGEN BONDED SUPRAMOLECULAR AGGREGATES IN THE SOLID LATTICE AND IN THE MESOPHASES

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Synthesis of new molecular building blocks to design supramolecular structures in the solid lattice and in solution has recently attracted great attention. Weak intermolecular interactions such as hydrogen bonding and van der Waals interactions are important to control molecular self-assembly in various phases. We are interested in pursuing this goal to achieve desired structure in the solid lattice and in the liquid crystalline phase using simple molecular and polymeric models. Two molecular models are explored as possible building blocks. The first one involves 5-alkoxyisophthalic acid (1) derivatives and the second one is based on bis(alkoxy)terephthalic acid (2).



Here the approach focus on two aspects:

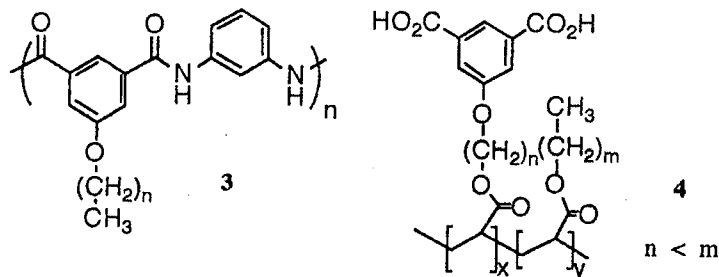
1) preserving the hydrogen bonding motif (i.e. dimerisation) of the diacid molecules and at the same time incorporate various additional interactions such as alkyl chain crystallization and other polar and nonpolar functional groups on the alkyl chain. The talk will concentrate on

- i) Self-assembly of the above mentioned building blocks in the crystal lattice
- ii) The effect of alkyl chain crystallization
- iii) The presence of polar and non polar functional groups on the alkyl chain.

2) manipulating the hydrogen bonding motif of the bifunctional dicarboxylic acid by adding bifunctional hydrogen bond acceptors. The resulting structure entirely depends on the nature and orientation of the hydrogen bond acceptor sites on the molecular components. A few examples will be given to show the self-organization of the diacid molecules in the crystal lattice in presence of bifunctional hydrogen bond acceptors.

The above mentioned diacids with long alkyl chains and their equimolar mixtures with bifunctional hydrogen bond acceptors show liquid crystalline behavior. Full characterization of the LC behavior using polarized optical microscopy, DSC, X-ray and the solid state NMR will be given.

Structural organization of macromolecules in the solid lattice can also be controlled using weak interactions. Here we demonstrate our goal using functionalized poly(isophthalamide)s (3) and polyacrylates (4) as model compounds.



Synthesis and structural characterization of these macromolecules will be discussed with examples.

Theory of Ionizable Polymer Brushes

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The mean-field theory describing the conformation of an ionizable polymer chain (weak polyacid or polybase) grafted at one end onto an impermeable planar surface and immersed into a water-salt solution is presented. The dependences of the brush thickness and degree of chain ionization on grafting density and ionic strength of the solution are analyzed. It is shown that the annealing of the brush affects the brush structure mostly at low ionic strength of the solution and relatively sparse grafting. The nontrivial effect of an increase in the brush thickness with decreasing grafting density and/or increasing ionic strength is predicted.

Charge Density Dependence of Correlation Length in Polyelectrolyte Solutions

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ABSTRACT: The electrostatic correlation lengths ξ in salt-free polyelectrolyte solutions have been measured as functions of charge density and polymer concentration using a small-angle X-ray scattering (SAXS) technique. In this case a water-soluble poly(vinyl alcohol) (PVA) was employed as a parent polymer to avoid increasing hydrophobic interactions with decreasing the charge density; partially sulfuric-acid esterificated PVA's were used as samples. The charge density defined by degree of esterification α was changed from 0.008 to 0.499. It was found that the maximum position q_m of a characteristic SAXS peak, which is attributable to the electrostatic interchain correlation, is proportional to the square root of polymer concentration C at any charge density as far as the solution is in the semidilute region. This supports that the isotropic model by de Gennes et al. is valid. The α dependence of q_m agreed with the theoretical prediction from a blob chain model for weakly charged polyelectrolytes proposed by Pfeuty and Khokhlov. Thus, it was experimentally shown that when the counterion condensation does not take place ($\alpha < 0.3$), the relation $q_m \sim \xi^{-1} \sim \alpha^{1/3} C^{1/2}$ is valid for semidilute solutions. This also indicates that the charge density dependence of correlation length can be understood within a framework of the isotropic model.

CONFORMATIONAL TRANSITIONS IN POLYELECTROLYTE RESPONSIVE GELS

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Polyelectrolyte gels swell intensively when immersed in the excess of water, and undergo sharp conformational transition (collapse of a gel) upon effective decrease of the solvent quality (addition of organic solvent, surfactants, linear polymers etc.). Collapsed gels, as well as the swollen gels near the point of conformational transitions exhibit complicated microstructures. In the present talk I will describe the experimental and theoretical results which were recently obtained in our laboratory in studying collapse of polyelectrolyte gels and emerging microstructures.

Microstructures in the collapsed gels may be due to the three competing reasons: a) polyelectrolyte/hydrophobic or polyelectrolyte/poor solvent interplay; b) ionomer-type multiplet structure formed by ion pairs; c) formation of kinetically frozen structures due to partial vitrification. These three reasons will be analyzed theoretically, and the results will be compared with experimental findings.

When a polyelectrolyte gel interacts with oppositely charged surfactants dissolved in the external solution, the effective absorption of the surfactants by the gel takes place. The concentration of surfactants inside the gel can thus easily exceed the critical micelle concentration (which is lower than in the external solution) and the micelles are formed in the gel. This process induces a gel collapse with the formation of highly ordered micellar self-assemblies inside the gel.

SELF ASSEMBLIES IN HYDROPHOBICALLY MODIFIED POLYELECTROLYTES

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Polyelectrolytes of polyacrylic acid type can be chemically modified by a simple grafting of a small content (a few molar percent) of very hydrophobic moieties such alkyl or perfluoroalkyl groups. In aqueous solution these macromolecules has an associative behavior. In dilute solution they show a coil-globule transition depending on the internal balance between a collapse tendency, governed by a micellisation type phenomenon of the hydrophobic substituents, and a chain expansion, modulated by the polyelectrolyte character.

In semi-dilute regime the hydrophobic microdomains play the role of reversible cross-links between the chains and a gel type behavior is observed. These microdomains are studied by various techniques, especially by the fluorescence of a pyrene probe.

The balance between collapse and expansion tendencies of the chains can be modulated by structural parameters :nature, size, ratio and distribution of hydrophobic substituents but also by external parameters such as pH or ionic strength.

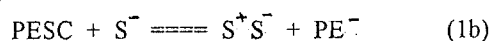
An other way to induce the formation of microdomains is to introduce surfactants or globular proteins in the polymer solution. Correlation between molecular structures and macroscopic behavior (rheology) are discussed

A Self-Assembly Phenomena in Multicomponent Systems Composed of Polyelectrolytes and Ionic Surfactants

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It is well known that the cooperative interaction between polycation (PE^+) and polyanion (PE^-) in water solutions leads to formation of a rather stable interpolyelectrolyte complexes (IPECs). Meanwhile, the cooperative interaction of PE^+ with anionic surfactant S^- (or PE^- with cationic surfactant S^+) in water media results in formation of stable polyelectrolytesurfactant complexes (PESCs). Actually, IPECs and PESCs formation is due to self-assembly of the complex particles from the components in water solutions.

We have studied for the first time a self-assembly phenomena in three-component systems composed of either PE^+ , PE^- and S^- or PE^- , S^+ and S^- . As it follows from ultracentrifugation and luminescence quenching data obtained, the PESC is more stable than IPEC while the complex (S^+S^-) formed by pairing of S^+ and S^- is more stable than PESC. The equilibria



proved to be completely shifted to the right at the concentration of S^- which was equal or lower than c.m.c.. The factors governing the equilibria 1a and 1b, in particular, the hydrophiliclipophilic balance of PE and S molecules as well as the nature of their ionic groups have been revealed. It was shown that the direction of the reactions is drastically dependent on the value of pH, ionic strength and the nature of added low-molecular weight electrolyte, i.e. on the factors which determine the electrostatic interactions between oppositely charged species $PE^+ - PE^-$, PE^+S^- and $S^+ - S^-$.

Temperature and a composition of mixed water-organic solvent, i.e. the factors which are able to affect on hydrophobic interaction between non-polar parts of S molecules and between these groups and hydrophobic fragments of PE chains proved to be also very powerful tools of the equilibria control.

The reaction 1a with the participation of oligomeric cations was also studied. The possibility of the equilibrium shifting to the right by means of PE chain shortening was demonstrated.

Polyelectrolyte-surfactant complexes: highly ordered microphase separated polymers

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Polyelectrolyte-surfactant complexes form spontaneously and in a well defined way by simple addition of polyelectrolytes and oppositely charged surfactants. This self-assembly process is highly cooperative and follows a strict 1:1 stoichiometry.

Since these molecules consist of a polar backbone (a string of ion pairs) on the one hand and the hydrophobic tails on the other, a demixing in the solid state and a connected mesophase formation are to be expected. Like in standard surfactant phases, the correlation length of these mesophases is related to the surfactant geometry and is of the order of $2 \text{ nm} < \xi < 8 \text{ nm}$. The actual structure type (cubic, lamellar or cylindrical) results from a delicate balance of the volume fractions of ionic and alkyl-mesophase and of the absolute amount of interface. The diversity of phase modifications is so large that most of the known morphologies of the complexes examined so far are different, and just some examples can be given.

The complex between polyacrylic acid and dodecyltrimethylammonium-counterions (PAA- C_{12}), exhibits a columnar morphology with localized cubic undulations along the cylinders ("frustration effects" or Landau Peierls instabilities). The series of complexes between polystyrenesulfonate (PSS) and various alkyltrimethylammonium - counterions (C_{12} - C_{18}), show a principal lamellar morphology, but exhibit different interface undulations which are fine-tuned by the relative volume fractions of both phases or the resulting spontaneous curvature of the interface. A plainly lamellar, a "mattress-phase" and a "perforated layer phase" are found.

The complex of natural lecithin and PDADMAC is a rubbery material ("plastic membranes") and exhibits a rather peculiar morphology where the stack of bilayers undulates with high amplitudes. Such complexes ("plastic membranes") combine the advantageous properties of natural bilayers (barrier and release properties) with those of polymers (stability, elasticity, processability).

Dynamics of Weakly Charged Polyelectrolyte in an Elongational Flow. Effect of Solvent.

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The scaling theory describing the behavior of a weakly charged polyelectrolyte molecule in an elongational flow field is developed. Salt-free and salt-added regimes at strong, theta and poor solvent conditions with respect to uncharged monomer interactions are considered. The dependences of critical flow gradient for stretching transition on the solvent strength and the ionic strength of the solution as well as on the degree of chain charging are analyzed. The region of salt concentration is determined where two critical values of flow gradient exist. The lower critical point corresponds to the stretching of a chain on the scale of superblobs of the size equal to the Debye screening length. The upper critical point corresponds to the complete stretching of a chain on the scale of monomer units. The influence of the solvent strength on the width of this region is shown. The diagram of states of a polyelectrolyte molecule in an elongational flow is constructed.

This work has been supported in part by the Russian Fundamental Research Foundation grant N0. 93--03--05797.

MICROSCOPIC INHOMOGENEITIES IN WEAKLY-CHARGED TEMPERATURE SENSITIVE POLYMER GELS AND SOLUTIONS

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The scattered intensity for weakly charged polymer gels of a poly(N-isopropyl acrylamide-co-acrylic acid) copolymer (NIPA/AAc) in deuterated water (660mM/32mM), $I(q)$, was obtained by means of small-angle neutron scattering (SANS) as a function of temperature and polymer fraction, ϕ , where q is the magnitude of the scattering vector.^{1,2} The scattered intensity was then compared with those for the corresponding polymer solutions. It was found that both structure factors were similar to each other and were well described with a Ornstein-Zernike type scattered intensity function when the temperature was lower than the so-called Θ temperature ($\Theta \approx 34.6^\circ\text{C}$) as shown in Figure 1. The correlation length, ξ , for NIPA/AAc solution was given by, $\xi \sim \phi^{-3/8}$, indicating a weakly charged polymer solution in a semidilute regime.³ On the other hand, no clear scaling law was obtained for NIPA/AAc gels. Above this temperature, both the gels and solutions started to have a peak at $q \approx 0.02\text{\AA}^{-1}$, which increased with temperature (See Figure 1). However, a significant difference in $I(q)$, due to the absence or presence of crosslinks, respectively for the solution and the gel, was observed at these temperatures. In the case of polymer solutions, a steep increase in $I(q)$ appeared by approaching $q = 0$, indicating a macroscopic inhomogeneity. On the other hand, $I(q)$ for polymer gels had a finite value at $q = 0$ due to the suppression of macroscopic inhomogeneity originated from the presence of crosslinks. A method to analyze these scattered intensity functions is proposed by comparing with the theory of Borue and Erukhimovich⁴ for polyelectrolytes in a poor solvent.⁵

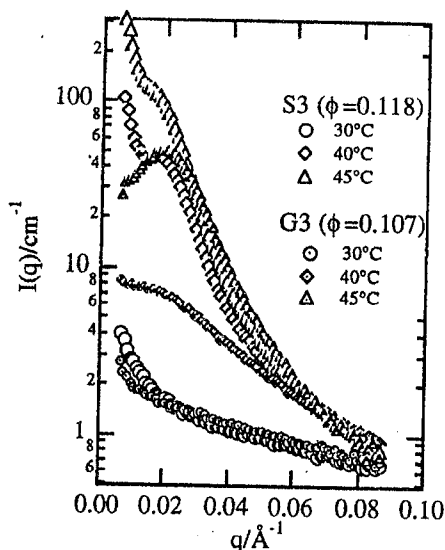


Fig. 1 Comparison of the structure factors of weakly-charged NIPA/AAc gel (G3) and solution (S3) at several temperatures.

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IONOMER-SURFACTANT SELF-ASSEMBLY IN LOW-POLARITY SOLVENTS.

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A systematic study of complexation reactions of sulfonated polystyrene ionomers having 1-5 molar percent of polar chain units with various oil-soluble surfactants is carried out in low-polarity organic solvents. It is shown for the first time that dipole-dipole attractions of the components lead to the formation of complexes characterized by limiting compositions and an unusual polymer-colloidal morphology of joint clusters and/or micelles. It is found that limiting compositions (ϕ) for the complexes formed between ionomers and/or surfactant of the same charge (bis(2-ethylhexyl)sulfosuccinate sodium salt), nonionic surfactants (primary aliphatic amines) are equal to 15-30 surfactant molecules per one ionomer salt/acid group on average, and ϕ depends on hydrophilic-lipophilic balance on the components, the initial aggregation state of surfactant and the nature of low-polarity solvent.

It is shown that ionomer-surfactant complexation is accompanied by disruption of self-contacts of ionomer salt/acid groups, which leads to "unfastening" and expansion of the ionomer coils in a dilute solution.

The "driving force" of the ionomer-surfactant complexation is related to:

- an increase of the system entropy due to "unfastening" and expansion of ionomer coils upon substitution of dipole-dipole self-contacts of ionomer salt/acid groups for their contacts with surfactant polar groups and
- a decrease in electrostatic component of the system free energy as the result of inclusion of the ionomer salt/acid groups into the joint clusters with surfactant polar groups.

In such complexes the ionomer salt/acid groups are playing role of the molecular "anchors", which efficiently bind reversed micelles and aggregates of surfactant, and induce aggregation of the molecular dispersed surfactant on the ionomer chain. A scheme of the structure of such complexes is put forward.

THERMOASSOCIATION OF POLYACRYLATE DERIVATIVES IN WATER.

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Most of water soluble polymers, used as thickeners to control the rheology of aqueous fluids, are characterized by a drop of viscosity when heated.

In order to overcome or to switch this main drawback, we developed a new family of amphiphilic polymers where self-assemblies are controlled by temperature.

This concept of 'thermoassociative polymers', based upon the loss of water solubility exhibited by some polymers above a critical temperature (L.C.S.T.), was exemplified with L.C.S.T. polyethers grafted onto hydrophilic backbones.

The overall behavior of such thermothickening systems can be depicted in a three steps mechanism according to the variation in viscosity with temperature.

In the lower temperature range, the copolymer solution displays a decrease of its viscosity upon heating as it is classically observed with usual water soluble systems.

When critical association temperature is reached, polyether side-chains are assumed to gather into 'hydrophobic clusters' and give rise, in a semi-dilute regime, to a dramatic enhancement of the viscosity. This latter can reach values of several order of magnitude higher than that of the precursor solution.

The last step of the rheological behavior, starts from the maximum of the viscosity enhancement with a continuous decrease with temperature, pointing out the loss of connectivity of the physical network. This phenomenon, related to a size increase of the microdomains (decrease of their number), can lead to a macroscopic phase separation at higher temperature.

This general feature, which can be managed playing either with the design of the copolymer (grafting ratio, nature and size of L.C.S.T. grafts, ...) or the solution parameters (concentration, ionic strength, ...), will be discussed here.

THE NONLINEAR CHANGE IN CONFORMATION OF POLYELECTROLYTE MACROMOLECULES IN SALTLESS WATER-ORGANIC SOLVENT

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High molecular weight polyelectrolyte: poly(dimethylaminoethylmethacrylate) [PDMAEMA] with molecular weights $M_w = 28.0 \times 10^6$, 20×10^6 , 15×10^6 was investigated in dilute solution by light scattering, flow birefringence, diffusion and viscometry (at different rate gradient) in a water-acetone system by varying the weight fraction of acetone " γ " in the mixture.

At $\gamma = 0.76$ the polymer undergoes a reversible coil-globule transition accompanied by a drastic decrease in intrinsic viscosity $[\eta]$, mean-square radius of gyration $\langle R^2 \rangle \propto z^{1/2}$, hydrodynamic radius R_h and second virial coefficient A_2 , with no change in molecular weight. The coil asymmetry parametre p ($p=2.5$ at $\gamma = 0.50$) decreases with increasing γ and attains unity (completely symmetrical particle) at the transition point ($\gamma = 0.76$).

The anomalous behavior of the viscosity of PDMAEMA-water-acetone solutions, detected near the transition point ($\gamma = 0.6 \div 0.7$), is interpreted by formation of local knots of compactization on the molecular chain under the influence of a hydrodynamic field.

Globule model is proposed for the polymer and compared with the models for polymers exhibiting different balance of electrostatic and hydrophobic interactions.

DYNAMIC SCATTERING FROM COMPLEXE
POLYMERIC SYSTEMS

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We discuss the dynamic scattering properties of complexe polymeric systems (polymer mixtures, copolymers and polyelectrolyte solutions) and emphasize how the mobility of the chain and the interaction parameters which control the dynamic and the thermodynamic of the system can be extracted. Some results using scattering techniques (light and neutron) are presented to illustrate the general behavior and under which conditions those quantities are measured. This is a direct consequence of considerable efforts made during the past decade, in the understanding of dynamic properties of multicomponent polymeric systems from both theoretical and experimental points of view.

Interactions Between Polymer Molecules and Lyotropic Liquid Crystal Phases at Concentrated Surfactant Solutions

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Abstract

While behaviours of hydrophilic polymers in dilute surfactant solutions ($<1\%$) have been well studied [1—3], the knowledge of interactions between polymer chains and surfactant molecules at high concentration phase is very limited. It is well known that surfactant molecules dissolved in water form aggregates called micelle, as the solution concentration is above CMC ($10^{-2} \sim 10^{-5}$). Factors responsible for micelle shape are intermolecular interactions at the micelle surface and alkyl chain packing within the micelle interior. Increasing surfactant concentration may change the globular shape of micelle to the long rod ones. It will lead to the formation of mesophase-lyotropic liquid crystals as the solution concentration is over 10%.

The interactions of polymer chains with mesophase of concentrated surfactant solutions have been studied at the present paper. Polymers used were PEO (Polyethylene oxide) and PAA (Polyacrylic acid), and surfactant chosen was SDS (sodium dodecyl sulfate). The solution concentration was ranged between 30~80%. The effects of polymer molecular weight, structure, and fraction in the solution on the textures of SDS liquid crystals have been studied under different conditions (Various shear rates, PH, temperatures, etc.), and a preliminary explanation for the interaction mechanism was proposed.

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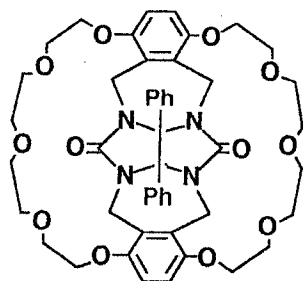
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THE DEVELOPMENT OF POLYMERIC PARAQUAT HOST-GUEST COMPLEXES

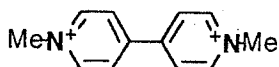
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Earlier research in our group led to the development of basket shaped molecules capable of binding neutral aromatic guests, alkali metals and quaternary ammonium ions. We have recently found that these basket shaped hosts (1) are also ideal receptors for the binding of the redox active species paraquat (2). The paraquat molecule complexing within the cleft of the basket.

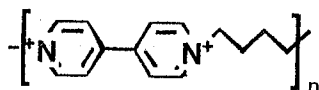


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Polymeric 'Viologens' (3) have previously been investigated as redox active films and more recently as optical data storage materials and show a wide variety of electrochromic and thermochromic behaviour. The binding properties of the basket molecule (1) to a series of polymeric viologens have been studied. The average molecular mass and electrochemical behaviour of the polymers (4) being modified by complexation.



3



4

INTRAMOLECULARLY-HYPERCROSSLINKED POLYSTYRENE A NOVEL MACROMOLECULAR NANO-SPECIES

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Starting with a technical polystyrene with an average molecular weight of 300,000 and a broad molecular weight distribution, synthesis protocols for obtaining intramolecularly hypercrosslinked polystyrene have been optimized. Most convenient seems to be a two-step process of chloromethylation of the linear polymer followed by the reaction of the chloromethyl groups with sterically accessible phenyl rings (i.e., intramolecular crosslinking) in a highly diluted solution.

Therefore, a monodisperse polystyrene standard with a mass of 330,000 was subjected to chloromethylation and intramolecular crosslinking. The product was further purified using preparative chromatography on a silica gel column in tetrahydrofuran. It was confirmed that the crosslinking of the polystyrene coils under optimized conditions mainly takes place intramolecularly. The main fraction of the product, when dissolved in tetrahydrofuran, results in a solution of a minimum viscosity (less than 0.1 dl/g), anomalously large sedimentation constant (32.6 Sv) and diffusion constant ($5.4 \times 10^{-7} \text{ cm}^2/\text{s}$) of the macromolecules and low partial specific volume.

A tendency for association was observed in solution, which renders the average molecular weights, determined by elastic light scattering and ultracentrifugation, relatively high (420,000 instead of 350,000). Using dynamic light scattering and exclusion chromatography, sizes of individual molecular species were found to exactly correspond to the value of 170 Angstrom which is expected for the molecule of 350,000 in weight and swelling coefficient of 3 in the solvent used.

When in dry state, the new polymer exhibits an unusually low density (about 0.7 g/cm^3), enormous inner surface area (about $1000 \text{ m}^2/\text{g}$) and the ability to increase in volume by a factor of 3 in any non-solvent for polystyrene.

Thus, novel molecularly dispersed polymeric species have been synthesized which should be referred to as "nanosponge". On the one hand, this name gives a reference to the molecular dimensions of the new particles (dozens to thousands of Angstrom). On the other hand, the above name associates with the open-work structure of the new species, a certain combination of its rigidity and flexibility, as well as its ability to accommodate large amounts of any solvent and non-solvent.

A remarkable tendency for formation of regular associates (clusters) has been discovered in the tetrahydrofuran solutions of the intramolecularly hypercrosslinked monodisperse polystyrene.

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NANOINHOMOGENEITIES IN POLYMER NETWORKS

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Small-size inhomogeneities (of the order of tens of nanometers) in polymer networks characterized by spatial differences in composition are formed as a consequence of history determined linking of units differing in some property into sequences (topological inhomogeneities), or by association (segregation) of units of different types, or by combination of both processes. Mixtures of long and short chains crosslinked with a common crosslinking agent, or multicomponent networks composed of "hard" and "soft" units serve as examples of topological inhomogeneities. Formation of silica clusters within a (crosslinked) organic matrix is an example of inhomogeneities formed by partial segregation. Crosslinked mixtures of more and less polar components (e.g. polyurethane network based on polybutadiene diols and poly(oxypropylene) triols) is an example of the combined formation of inhomogeneities. These inhomogeneities can be characterized by scattering methods.

For modelling of the topological inhomogeneities, simple mean-field models based on the statistical theory of branching processes (TBP) can be developed and degree of polymerization averages of these inhomogeneities or their functionality averages (e.g. number of soft chains issuing from a hard cluster) can be calculated in dependence on the initial composition, reactivities of the functional groups, or history of network formation (staging). Such characterization is possible by distinguishing bonds between e.g. soft-soft, soft-hard, and hard-hard units and their multiplicative probabilities. This is a basic information for comparison with experiments and represents the effect of chemistry. Deviations are due to segregation or diffusion effects. More sophisticated models view inhomogeneities formation as a kinetic process where effective reactivity of functional groups in reactions, by which inhomogeneities are formed, depends on the size, composition, and connectivity pattern of the given inhomogeneity. Among these, Monte-Carlo simulations based on generalized kinetic differential equations of Smoluchowski type are being developed at present.

Theory of Dielectric Relaxation in Polymer Networks with Different Structure

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The theory of dielectric relaxation of polymer networks built from polymer chains with longitudinal component of dipole moment for simplified models of polymer networks is proposed. The nush-like and tree-like networks are considered. If the lengths of the initial chains included in the network structure are longer then the distance between the junctions the dielectric relaxation properties are determined with the long-range relaxation spectra. The characteristic times and shape of these spectra depend on the chain lengths between the junction and on the dimensionality, functionality and type of connectivity of the network. The effects connected with the restricted mobility of the junctions are discussed.

**Inorganic/Organic Composite (Interpenetrating) Polymer Networks
Based on Zeolite 13X and Polystyrene and Polyethylacrylate**

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Abstract

A hybrid inorganic/organic composite (interpenetrating) polymer network (IPN) of a three-dimensional network structural zeolite crystal (13X, powder) and cross-linked or linear polystyrene (PS) was prepared and characterized by DSC, solid-state ^{13}C -NMR, and SEM. The size and shape of the crystalline zeolite particles were revealed on SEM micrographs in both the pure zeolite and the IPN's. Solubility tests and the results of DSC with solid-state ^{13}C -NMR confirm that some organic PS chains are incorporated within the internal three-dimensional channels of the zeolite particles. We speculate that the internal PS chains may adopt an extended "one-dimensional" conformation. Thus solvent extracted linear PS/zeolite samples lost most of the zeolite surface held PS chains but not all the PS and exhibited a DSC curve similar to the unextracted sample with no PS glass transition of any kind. Similar results were obtained with rubbery linear and crosslinked polyethylacrylate (PEA)/zeolite composites. Again the extracted linear PEA/zeolite composite, which appears to retain PEA in the pores or the zeolite, exhibits no glass transition temperature. Further dielectric constant, small angle X-ray and neutron scattering experiments are underway. In any case this appears to be a novel class of hybrid inorganic-polymer composites.

COMPARISON OF ASSOCIATION PROCESSES IN PHYSICAL GELS AND IN POLYMERS WITH SMALL NUMBER OF STICKERS

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It is shown by Russian scientists (V. Kargin and co.) that the association processes, i.e. the formation of supramolecular structure are typical of polymers and their solutions independently of the polymer structure; they are caused by high molecular weight of the polymers and, consequently, their high viscosity, the both factors being favourable for the formation of the fluctuation network.

However, only the existence of highly interacting functional groups (HIFG) in macromolecules predetermines the formation of a stable rubber-like physical network, which is characteristic both of physical gels and of flexible polymers with small number of stickers.

Two types of intermolecular interactions are inherent of physical networks of any types: interaction between chains and HIFG, whereas the latter have to be stronger than those between HIFG and solvent molecules. The quality and selectivity of the solvent is the determining factor in the association processes.

Polymer physical networks are characterized by the different phase state as well as different morphology of the phases. They can be formed: 1) as a result of macrophase separation (up to colloid system in a very poor solvent); 2) microphase separation (with domain or cluster formation); 3) formation of local point contacts and consolidation of macromolecules in the framework of one-phase system.

Specific mechanism of physical network formation is the competition between intra- and intermolecular bonds formation and the rearrangement of intra- to intermolecular bonds due to the changes of thermodynamic conditions.

All steps of the intra- and intermolecular binding processes are exhibited in the change of the rheological properties of the systems, namely their viscosity, rubber-like elasticity and the complex of relaxation parameters.

This paper represents the experimental data of the authors, which illustrate the above ideas by the examples of polymers differing in the structure, the amount of HIFG, chain rigidity and solvent quality: the gels of gelatin, poly(vinyl alcohol), oligocarbodiimides, poly(amidhydrozide), as well as the networks of poly(dimethylcarbosiloxanes) with small number of side COOH groups. In particular, it is shown for hydrogels of gelatin whose network is stabilized by hydrogen bonds and hydrophobic interaction, that gradual addition to water of formamide (which destroys hydrogen bonds), and DMSO (which prevents hydrophobic interaction) leads to the destruction of the gel and to the formation of the solution with high rubber-like elasticity. The change of association character results in the variation of the elasticity modulus of the system on four orders of magnitude and the viscosity - on eight orders of magnitude.

STATISTICAL PHYSICS OF POLYMER GELS

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This work presents a comprehensive analysis of the statistical mechanics of randomly cross-linked polymer gels made of phantom chains with excluded volume, starting from the general model and ending with analytic expressions for density correlation functions which can be tested by scattering experiments. Using replica field theory we construct and solve the mean field equations and show that the ground state is described by a solution with spontaneously broken symmetry with respect to translation in replica space. The mean field thermodynamic free energy is derived and is renormalized by short wavelength fluctuations which introduce wasted loop corrections into the classical theory of polymer networks. The mean field solution contains statistical information about the behavior of individual chains in the network and, in particular, about the deviations from affine response to deformation.

We calculate the spectrum and the eigenfunctions which describe long wavelength fluctuations about the mean field solution. We derive the non-averaged free energy functional of the density field and of a Gaussian random field which represents the quenched inhomogeneous structure of the gel. This free energy can be used to obtain all the statistical information about the density fluctuations in a deformed network, in terms of the average number of cross-links and the thermodynamic parameters (temperature, density and quality of solvent) of the initial and the deformed states. We calculate the density correlation functions which describe quenched and thermal density fluctuations. Analytic expressions for the correlators are obtained in the continuum, mesoscopic and short wavelength limits. The connection with the usual theories of elasticity of solids is discussed and it is shown that a stretched network is a solid with strain-dependent anisotropic elastic modulus. This anisotropy, together with the quenched heterogeneous structure of the network, leads to the butterfly patterns observed in neutron and light scattering from stretched gels.

Our model is applied to the case of free labelled chains in a network and the corresponding structure factors are calculated and analyzed in detail. Using renormalization group and scaling methods, we generalize the theory to the case of gels in good solvents and calculate the thermodynamic free energy, the moduli and the density correlation functions. Throughout this work we compare our predictions to the results of scattering experiments on deformed polymer networks.

INTERFACIAL TENSION OF A DEMIXED A/B POLYMER BLEND WITH A-B DIBLOCK COPOLYMER NEAR THE CRITICAL POINT

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Effect of A-B diblock copolymers on the interfacial tension of a demixed homopolymer A/B blend should depend on the segregation strength of the blend. Near the critical consolution temperature, the presence of diblock copolymers must give a weak change to the interfacial tension, whereas, at strong segregation away from the critical point, it must appreciably reduce the interfacial tension owing to adsorption of the copolymers at the interface. Therefore, it is expected that one can see the crossover from the weak to the strong reduction of interfacial tension upon cooling (going away) from the critical temperature, where the interfacial tension possibly exhibits a maximum in its temperature dependence. In this study, this expectation is investigated theoretically and experimentally. A simple theoretical consideration is made on the basis a mean-field treatment, where are taken into account two dominant factors only, localization entropy loss and segmental interaction gain with adsorption of the copolymers. The theory predicts the crossover with the maximum for addition of a small amount of diblock copolymers having a polymeric index larger than those of homopolymers. Temperature at the maximum moves closer to the critical point as the copolymer concentration is increased. Consistent experimental results are obtained for a demixed oligo(styrene)/oligo(dimethylsiloxane)(OS/PDMS) blend with poly(styrene)-*block*-poly(dimethylsiloxane)(PS-*b*-PDMS), as shown in Figure 1. Theoretical results corresponding to the experiments are shown in Figure 2.

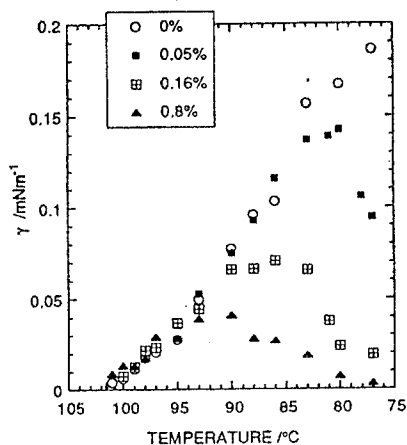


Figure 1 Interfacial tension γ of OS ($M_w=600$)/ODMS($M_w=460$) with PS-*b*-PDMS($M_w=9900$) of indicated concentrations near the critical temperature T_c .

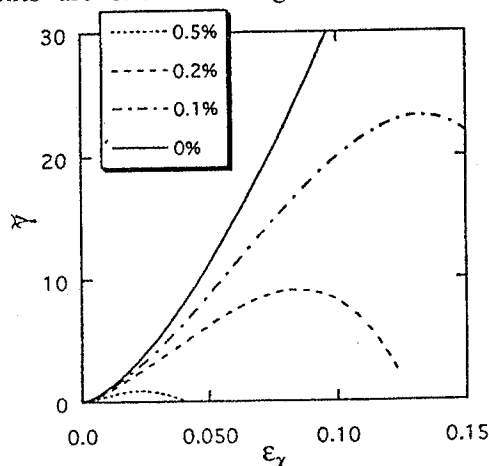


Figure 2 Scaled presentation of theoretical curves of interfacial tension against temperature distance from T_c .

PHASE BEHAVIOR OF, AND INTRAMICRODOMAIN BLOCK SEGREGATION IN, PERFECTLY-ALTERNATING (AB)_n MULTIBLOCK COPOLYMERS

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Synthesis of perfectly-alternating (AB)_n multiblock copolymers affords a unique opportunity to examine intramicrodomain block segregation based solely upon conformational constraints and the effect of such segregation on both phase behavior and ultimate thermo-mechanical properties. In this work, a series of symmetric (50/50 wt%) poly(styrene-*b*-isoprene)_n (SI)_n multiblock copolymers with $1 \leq n \leq 4$ and either (i) constant block lengths or (ii) constant chain lengths have been synthesized through sequential anionic polymerization and have been characterized by transmission electron microscopy, small-angle x-ray scattering and differential scanning calorimetry. Results from these studies are used to diagnose the phase behavior of the copolymers as a function of block pair (*n*), as well as the conformational properties and intra-microdomain segregation of both the end- and mid-blocks. A self-consistent field treatment which extends the work of Zhulina and Halperin (*Macromolecules* 25, 5730, 1992) and Jones *et al.* (*Chem. Eng. Sci.*, in press) for lamellar triblock copolymers is proposed to deduce such properties by explicitly including the 2*n* endblocks and 2(*n*-1) midblocks which must all reside within a lamella. Predictions of microstructural dimensions (e.g., microdomain periodicity) are found to compare well with experimental data, supporting the expectation that the fraction of bridged midblocks in microphase-ordered multiblock copolymers is strongly dependent on *n*.

MORPHOLOGY AND DOMAIN SIZE OF A MODEL GRAFT COPOLYMER

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Morphologies and domain sizes of block copolymers have been extensively studied by using well-defined samples. However, few basic studies were reported on graft copolymers, whereas they are widely used in industry. In this work, therefore, we prepared a well-defined graft copolymer of which a graft chain (polystyrene (PS)) grows at the center of a main chain (poly(2-vinylpyridine) (PP)) as a model sample by an anionic polymerization technique and studied the variation of morphology with composition and the molecular weight dependence of lamellar domain spacing in comparison with those of diblock copolymers.

The graft samples were prepared by successively coupling a living PS and two living PP's with 1, 3, 5-tris(bromomethyl)benzene (TB). The intermediate (PS-TB) and final products were purified by fractionation and extraction. The film specimens were prepared by casting from tetrahydrofuran solutions and annealed in vacuum at 150 °C. The morphologies of samples were examined by transmission electron microscopy and small-angle X-ray scattering (SAXS) and the lamellar domain spacings were measured by SAXS.

The variation of morphology with the volume fraction of PS graft chain ϕ_{PS} is similar to that of diblock copolymers, but the morphological changes occur at the ϕ_{PS} values larger than those of diblock copolymers. The molecular weight dependence of lamellar domain spacing is similar to that of diblock copolymers, but the magnitudes are smaller than those of diblock copolymers with the same molecular weights. These results can be well explained by the difference in the molecular architectures of graft and block copolymers.

Statics and Dynamics of ω -Functionalized Block Copolymers of Styrene and Isoprene

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Abstract

The statics and dynamics of ω -functionalized diblock copolymers of styrene and isoprene have been studied with small-angle X-ray scattering (SAXS) and with rheology and dielectric spectroscopy, respectively. The asymmetric diblock copolymers ($w_{PS} \approx 30\%$) had a dimethylamino or zwitterion groups at either end of the chain and the molecular weights were in the range $0.62\text{--}2.44 \times 10^4$ g/mol. Depending on the temperature, the SAXS results revealed two separate levels of microphase separation: one between the polystyrene (PS) and polyisoprene (PI) blocks forming the microdomain structure and another one between ionic and non-ionic material. The latter process creates sufficient contrast notwithstanding the small fraction of the zwitterionic groups. When the zwitterion is linked to the PI chain-end aggregates are formed at low temperatures within the PI phase. These aggregates manifest themselves both in rheology and in dielectric spectroscopy, respectively, with an extended rubbery plateau and with a new dielectric process associated with restricted PI segmental relaxation. When the zwitterion is located on the PS chain-end association takes place, at high temperatures, within the PS phase and act as to stabilize the new microdomain up to very high temperatures. When compared with neutral diblocks, the ω -functionalized diblock copolymers constitute a *new* class of materials which provide the possibility of altering the *phase behavior* by introducing a small amount of a polar group at one chain-end.

EFFECT OF MONOMER SEQUENCING ON THE EQUILIBRIUM PHASE BEHAVIOR OF BLOCK COPOLYMERS AND THEIR BLENDS

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The phase behavior of AB diblock copolymers is dictated by the thermodynamic incompatibility χN (where χ is the Flory-Huggins interaction parameter and N denotes monomer number) and the molecular composition f_A . Since most studies of block copolymers have focused on those comprised of styrene (S) and isoprene (I) monomer units, it is useful to retain these chemical species in comparative studies. A shortcoming in this vein, however, is that χ , at a given temperature and composition, is fixed. To overcome this drawback, we have examined ordered and disordered block copolymers wherein at least one block is a random poly(styrene-*r*-isoprene) segment. Employing a unique co-catalyst polymerization route, random blocks of block copolymers can be generated in which no composition gradient exists along the backbone. One of the copolymers studied here, a diblock copolymer possessing symmetric 75/25 and 50/50 (wt%) S/I blocks, is disordered at ambient temperature. Addition of homopolystyrenes varying in molecular weight provides a look into phase segregation in the disordered state. Another series of copolymers with a 50/50 (wt%) S/I random mid-segment of weight fraction Φ resembles "tapered" block copolymers. In contrast, however, the mid-segment in each of the copolymers studied here possesses constant composition. Microdomain periodicities measured with transmission electron microscopy and small-angle neutron scattering are correlated with Φ and compared with predictions from a self-consistent field theory (Kane and Spontak, *Macro-molecules* **27**, 1267, 1994) to deduce $\chi(\Phi)$. Moreover, blends of these lamellar copolymers with low-molecular-weight homopolystyrene produce different morphologies, depending on Φ .

Adsorption of Linear Homopolymers: Equilibrium and Dynamics

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Abstract. Properties of polymer layers adsorbed from a good solvent onto a solid wall are considered theoretically. It is shown that under saturation conditions the tails of polymer chains create an important contribution to the monomer density far from the wall: the tail part dominates in the region $aN^{0.5} < z < aN^\nu$ where z is the distance from the wall, a is the link size, and ν is the Flory exponent. Thus it is the tail properties that determine the total layer thickness.

Dynamics of unentangled adsorbed layers is also considered. Here it is shown that: (i) the bottleneck for adsorption of a new chain onto the solid wall (which is already covered by polymers) is the stage of "critical" spreading corresponding to creation of G contacts with the wall with total binding energy of order of kT ; (ii) the process of exchange between labeled adsorbed chains and unlabeled chains in solution is slower than a formation of a saturated layer, but is much faster than the desorption process. The molecular weight dependencies for characteristic times of these processes are predicted.

THE STRUCTURE OF THE INTERFACE BOUNDARIES IN POLYMER SYSTEMS AS REVEALED BY SMALL-ANGLE X-RAY SCATTERING

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Small-angle X-ray scattering (SAXS) is a useful technique to investigate the fine inner structure of different polymers on a scale from about 0.5 nm through 200 nm. A main advantage of this technique is its ability to incorporate a large volume of material into a single experimental scan, thereby providing statistically averaged measurements of the total volume, surface area and size of scattering centers.

In SAXS method the information of the interface structure in the nanoheterogeneous polymer system can be obtained by measurements of the scattered intensity in the relatively large scattering angle region known as Porod's region followed by an appropriate mathematical data treatment.

At the present time there are many different approaches for learning about the interface structure in polymer systems, starting with the classical model that treats the interface as if it is a smooth wall and ending with the fractal concept. However, the description of the interface in the specific polymers remains still to some extent questionable.

In this work a number of polymer systems, namely, semi-crystalline polyolefines, ionomers, statistical polyblock copolymers, super-crosslinked networks, metal polyoxides and dendrimers were studied in order to obtain the information about the interface structure and to define the feasibility of that or those approaches.

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SCANNING FORCE MICROSCOPY IN SURFACE ANALYSIS OF POLYMERS

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Scanning force microscopy (SFM) provides unique possibilities for the analysis of polymer surfaces. It allows to examine topography, nanostructure, mechanical and other surface properties. The most important aspect of SFM of polymers is the optimization of experiment to provide high-resolution imaging at different applied forces ¹. This can be achieved by employing different modes (e.g. contact mode, lateral force mode, tapping mode) and by conducting measurements in various environments (e.g. in air, in dry nitrogen, under liquid). Minimization of the applied force is needed to avoid the damage of weakly-bound surface structures and to improve the resolution of nanoscale features. Force-dependent imaging helps to distinguish surface regions with different hardness and to separate topographical and mechanical contributions to the SFM image.

Low-force imaging of polymer surfaces allows to detect nanoscale structures that are not accessible by other microscopic techniques. Particularly, on samples of stretched ultra high molecular weight polyethylene (PE) we observed surface layers of nanofibrils (2-3 nm in width) oriented in and perpendicular to the stretching direction ². We also were able to image directly sectorization borders and nanoscale grains of the lamellar surface of polymer single crystals ³. Generally the advanced structural analysis in the nanoscale with SFM ⁴ is more important than the ability of this method to detect periodical molecular and chain order.

In contrast to the low-force imaging, one may deliberately employ strong repulsive forces to examine an elastic, plastic or viscoelastic response of polymer surfaces. At elevated forces periodical contrast variations along the fibrils appear in the images of stretched samples (PE, polypropylene, nylon). These variations coincide with the *long period* from diffraction experiments and are related to an alternation of hard and soft regions in the 10-30 nm range. Molecular-scale images of stretched PE reveal that the hard regions consist of arrays of extended polymer chains whereas the soft domains are less ordered. Therefore the contrast of the high-force images is caused by different responses of surface regions to the tip-force.

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X-RAY AND NEUTRON REFLECTIVITY STUDIES OF LANGMUIR-BLODGETT FILMS CONTAINING POLYMERS

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An introduction to the methodology of X-ray and neutron reflectometry is given in which the fundamental aspects regarding the performance of specular reflecton measurements and subsequent analysis of the data.

Neutron and X-ray reflectivity measurements are used to characterize Langmuir-Blodgett films composed of twenty bilayers of barium stearate. To facilitate contrast for neutron measurements, molecules with deuterated aliphatic tails were used for the deposition of every odd-numbered bilayer. Model fitting of both data sets shows the following: the bilayer thickness, the area per molecule, the value of a mixture of Ba salts and undissociated carboxylic acid groups and that the neighboring bilayers are 30% intermixed. Structural changes of such films were studied during temperature annealing at 66 C. Interlayer diffusion and evaporation of matter were observed. Quantitative parameters of these processes were calculated.

Fabrication and X-ray reflectivity study of polymeric Langmuir-Blodgett films of copolymers consisting of hydrophobic flourocarbon monomers and small hydrophilic spacers are presented. Such a constitution is different from that of conventional amphiphilic compounds where hydrophilic and hydrophobic parts are in the same monomeric molecule. Complex Langmuir-Blodgett films consisting of alternating molecular layers of fluorinated (one of the above copolymers) and non-fluorinated (fatty acid salt) compounds were prepared. X-ray reflectivity study showed good stacking order of molecular layers in these films and allowed to calculate their electron density profiles.

X-ray reflectivity data for complexes of DNA with cationic amphiphilic molecules (octadecylamine or dioctodecyldimethyl ammonium bromide) prepared by Langmuir-Blodgett technology are presented. DNA molecules in Langmuir-Blodgett multilayers reveal two main forms: double -helix structure (complex with dioctodecyldimethyl ammonium) and single-stranded structure (complex with octadecylamine).

MOLECULAR FILM SUPERLATTICES ORGANIZED FROM OPPOSITE CHARGED POLYIONS (BIOLOGICAL, ORGANIC AND INORGANIC) BY MEANS OF ALTERNATE ADSORPTION

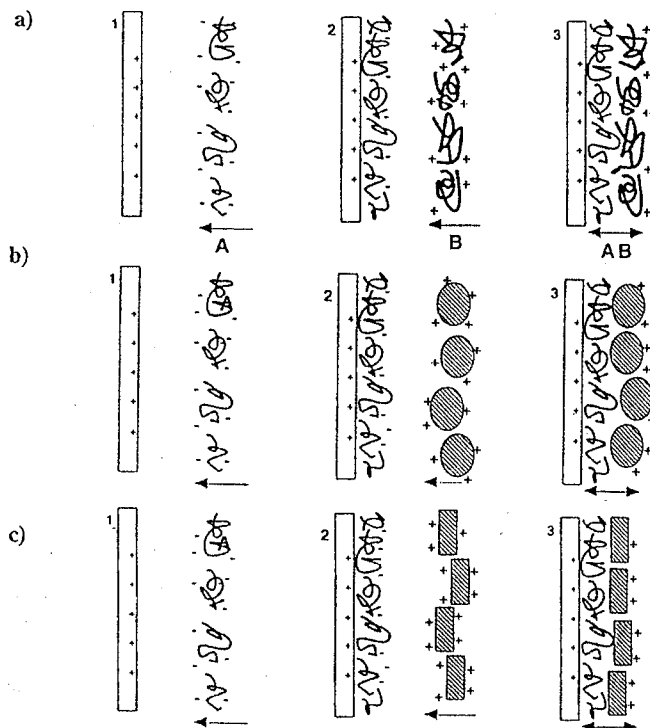
Yuri Lvov, Katsuhiko Ariga, Izumi Ichinose, Toyoki Kunitake
 Supermolecules Project, JRDC, Kurume Res. Center, Kurume and Faculty of Engineering,
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The assembly of ultrathin organized films on solid substrates by means of alternate adsorption of polycations and polyanions was invented for colloidal particles by Iler[1] and then developed for linear polyions by Decher and coworkers[2-3]. We generalize the procedure as based on re-saturated alternate adsorption[4] of oppositely charged polyions of different nature. The change of a film outermost charge to the opposite one at every consequent adsorption cycle is the key point of the procedure. The technique does not need drying of a sample and may be used for different kinds of charged particles, including biological: proteins, viruses, DNA[5-6].

In the Fig.1 we demonstrate simplified schemes of: a) Assembly by alternation of linear polyanions and polycations. b) Inserting in the multilayer at every even step of charged particles; 11 different globular proteins, CeO_2^+ and TiO_2^- nanoparticles were assembled in alternation with Na-poly(styrenesulfonate), poly(ethyleneimine) or Br-poly(diallyldimethylammonium). c) Alternating of linear polyions and preformed charged plates (de-laminated montmorillonite clay with dimensions $1 \times 500 \times 500 \text{ nm}$) was done also.

Control of the assembly process was performed with the help of quartz crystal microbalance technique (QCM), UV absorbency, small-angle X-ray reflectivity and scanning electron microscopy. QCM kinetic monitoring *in-situ* of an adsorption for variety of compounds shown, that 20 min is a sufficient time for re-saturation; linear polyions concentration higher than 0.002 M/l was necessary[4]. Combinations of all three modes of the assembly for complex superlattices production was demonstrated[6].

Figure 1:



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SELF-ORGANIZATION OF LIQUIDS AT INTERFACES AND IN THIN FILMS: A MOLECULAR DYNAMICS SIMULATION STUDY

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Interfaces between flat solid surfaces and complex fluids are of considerable academic and technical interest, in particular, in the context of adsorption, the formation and organization of molecular films. Molecular dynamics (MD) simulations are very well suited to study the underlying microscopic mechanisms of such phenomena. MD simulations provide detailed molecular pictures of the structure and dynamics of fluids in confined geometries. As an example, the structure and dynamics of *n*-alkane chains and benzene molecules at a solid-liquid interface are investigated. The simulations show that the structure of the molecules adjacent to a surface strongly depends upon the surface interaction. Well ordered liquid crystalline like monolayers covering an attractive, graphite like surface are found to be the most stable configuration. Similar stabilities are observed for 1,12-dodecandiol molecules adsorbed on the basal plane of graphite in a herringbone like structure. In contrast, reflecting surface systems exhibit no long range order for short *n*-alkanes. The conformational properties of molecules are primarily affected in the first two or three layers adjacent to a surface, although the local monomer density is modulated over a larger length scale. Investigations of the chain center of mass dynamics perpendicular to the surfaces reveal an anomalous, slowed down diffusion behavior for chains close to a surface. In contrast, chains in the vicinity of reflecting surfaces exhibit an increased mobility parallel to the surfaces, although the density is higher than in the bulk. This finding contradicts experimental results of fluids confined between solid surfaces, which exhibit an increased viscosity. Consequently, a subtle interplay between the surfaces modifies the liquid structure between them over a length scale which is larger than the one relevant for an isolated interface. An appropriate set up for the MD simulation of a confined liquid is suggested, where the equilibrium fluid density between the surfaces is governed by the chemical potential. The force versus separation of the surfaces curves for various liquid-surface interactions are calculated and compared with experimental surface force apparatus measurements. Especially, the self-organization of simple fluids in a confined geometry is discussed. In addition, the adsorption of *n*-alkanes from a nonpolar solvent onto a flat solid surface is presented, together with the early organization of the alkane chains at the interface. Our model system consists of liquid benzene confined within a narrow slit, with C₁₄H₃₀ alkane chains placed in its center. Chains diffusing within the range of the surface potential penetrate the highly structured benzene layers near the surface and adhere to the graphite surface. The chains adsorb flat against the surface, i.e., the molecular axis is oriented parallel to the graphite with no tails extending into the benzene. The adsorbed chains favor stretched configurations, with mean square end-to-end separations about 90% relative to the all-*trans* extension. Both findings are prerequisites for the formation of dense crystalline monolayers observed in scanning tunneling microscopy (STM) experiments. Furthermore, indications are found for the clustering and orientational ordering of the adsorbed chains.

**POLYMERIZATION AND MOLECULAR RECOGNITION IN THE
MONOLAYERS OF SYNTHETIC AND NATURAL COMPAUNDS**

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The surface-active properties and kinetics of the polymerization in monolayers of specially synthesized lipid-like monomers with polymerizable groups in the hydrophobic (diacetylene and butadiene monomers) and hydrophilic (acrylic, methacrylic, vinyl monomers) parts of molecules were investigated. It was found that the dependences of the polymerization rate vs. surface pressure for monomers of the first type had only one sharp maximum at middle values of the surface pressures (8-12 mN/m in the case of diacetylene monomers) and decreased at higher pressures. For the monomers of the second type - an additional minimum of the polymerization rate (at surface pressures about 5 mN/m in the case of acrylic monomers) was observed. The obtained effects were explained by differences in the nature and position of the polymerizable groups in lipid molecules, as well as their orientation at the interfaces.

These lipid-like monomers were used for the immobilization of peptides (like valinomycin) and proteins (like glucose oxidase). Using surface potential and Brewster angle reflection measurements, it was shown structural changes of the valinomycin-lipid monolayers during complexation with K^+ as compared to Na^+ and other cations. Glucose oxidase is considerably stronger adsorbed on positively charged lipid monolayers than on zwitterionic ones and only slightly - on negatively charged monolayers, because of the electrostatic lipid-protein interactions. By transfer of these lipid-protein monolayers onto Pt-electrodes under 20-40 mN/m surface pressure the biosensors were obtained with a measuring range of 0.5-5.0 mM glucose. The polymerization of these layers by soft UV-illumination at the interface increases the stability of the film and reproducibility of the response measurements.

ELECTRON DIFFRACTION STUDY OF THE STRUCTURE OF DIFFERENT KINDS OF LANGMUIR-BLODGETT FILMS

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At present various crystal structures have been determined by the method of electron diffraction structure analysis. Recently this method was successfully used for studying thin films formed by Langmuir-Blodgett deposition. In many instances (multilayer films of lead stearate, five homologues of tetraalkanoiloxhydroquinone, cholesterol, et al.) using of electron diffraction structure analysis provides a determination of the unit cell parameters, the structure of molecules and their packing in the layers. The structural studies of Langmuir-Blodgett films meet serious difficulties associated with the small sizes of molecular crystallites and with structural distortions such as shifts of molecules along their long axis, displacements in the side packings, and mutual tilts of the molecules. Films with higher degree of disorder were studied. An example is the Langmuir-Blodgett film, which is built by the aliphatic chain and diacetylene groupings, $\text{CH}_3-(\text{CH}_2)_{20}-\text{CO}_2-\text{CH}_2-\text{C}=\text{C}-\text{C}=\text{C}-\text{CH}_2\text{OH}$. In this case electron diffraction patterns show diffuse reflections only on the ellipses close to the pattern centre, whereas at large angles there are only amorphous halos.

Electron diffraction structure analysis allows to investigate Langmuir-Blodgett films consisting of molecules of different kinds, including, e.g. protein, DNA, and other molecules. One can also study by the electron diffraction structure analysis rearrangement of molecule packings, chemical reactions in Langmuir-Blodgett films, etc. For example, the reaction of imidization in the time of formation of ultrathin film of polyimide PM.

ON THE INFLUENCE OF HARD WALLS ON STRUCTURAL PROPERTIES IN POLYMER GLASS SIMULATION

Jörg Baschnagel and Kurt Binder

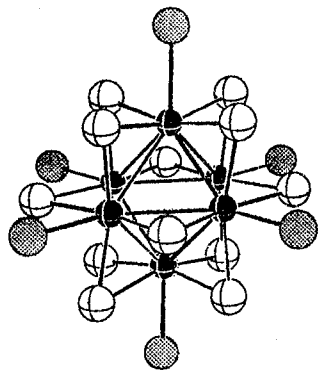
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Structural properties of a dense polymer melt confined between two hard walls are investigated over a wide range of temperatures by dynamic Monte Carlo simulation using the bond-fluctuation lattice model. The temperatures studied vary between those of the ordinary liquid to those of the strongly supercooled melt. At high temperatures the configurational properties of the polymers close to the walls exhibit the following features: The density profiles of the monomers and of the end-monomers are enhanced at the walls and decay towards the bulk value on the length scale of the bond. Both the bonds and the chains tend to align preferentially parallel to the wall. The radius of gyration is the largest length scale characterizing the extent of the interfacial region. When the melt is progressively supercooled all features of the profiles and the tendency of parallel orientation with respect to the walls become more pronounced. For the strongly supercooled melt the perturbation introduced by the presence of the walls penetrates deeply into the bulk, decaying on a length scale which is larger than the radius of gyration.

On The Chemistry Of Metal-Rich Niobium Halides

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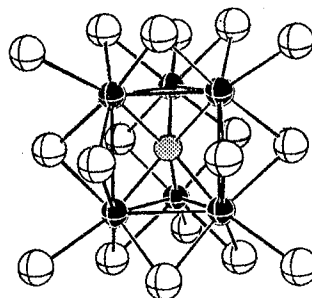
Explorative synthesis in the field of inorganic solid state and solution chemistry has provided us with a manifold of new ternary and quaternary compounds with interesting electronic and chemical properties. Some of these compounds are derivatives of the well known $[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]^{4-}$ building block [1].



$[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]^{4-}$

Starting from several new compounds with three-dimensional solid state structures, such as $\text{K}_2\text{Mn}[\text{Nb}_6\text{Cl}_{18}]$, $\text{CsTi}[\text{Nb}_6\text{Cl}_{18}]$, $\text{Li}_2\text{In}_2[\text{Nb}_6\text{Cl}_{18}]$ or $\text{Rb}_2\text{Cu}_2[\text{Nb}_6\text{Cl}_{18}]$ [2,3], $[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]^{4-}$ units can be extracted into solution and partially modified to become halide-pseudohalides like $[\text{Nb}_6\text{Cl}_{12}(\text{N}_3)_6]^{4-}$ or $[\text{Nb}_6\text{Cl}_{12}(\text{NCS})_6]^{4-}$ [4]. The latter can be crystallized with different alkali counterions and exhibit an extraordinary solution behaviour with organic solvents.

Solid state chemistry techniques have also lead to the discovery of new niobium cluster compounds. A novel sulfur centered trigonal prismatic niobium cluster is present in the structure of $\text{Rb}_3[\text{Nb}_6\text{SBr}_{17}]$ [5]. The electronic conditions for this compound can be derived from the Nb_3Br_8 structure [6] and are well understood.



$[\text{Nb}_6\text{SBr}_{18}]^{4-}$

More complex structures containing quasi one-dimensional chains have been discovered in $\text{Rb}[\text{Nb}_3\text{SBr}_7]$ [7] and $\text{Nb}_6\text{I}_9\text{S}(\text{Nb}_6(\text{H})_9\text{S})$ [8] with corresponding one-dimensional semiconducting properties.

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**POLYMER BIOMIMETIC SYSTEMS :
DESIGN, PROPERTIES AND APPLICATIONS**

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Polymer biomimetic systems (planar monolayers and bilayers, liposomes, micells, microspheres) are unique model of biomembranes, especially for investigation of the following processes : molecular self-organization and recognition , conformational structures and membrane transport, photoreception and so on. These systems are promising materials for nanotechnology, molecular electronics, biotechnology and medical diagnostics. The polymerization of surface-active monomers (SAM) in such systems is a very suitable method for preparation of stable ultrathin oriented membranes with desirable properties.

Polymerization of the specially synthesized lipid-like monomers: 1,2-ditetradeca-11,13-diinoylglycero-3-phosphorilcholine (TDPC), 1,2-di-(12-oxo-10-octadecenoil) glycero-3-phosphoril-choline (ODPC), N-acryloylphosphatidylethanolamine (ACPE) and N-methyl,N-buthyl,N-cetylacetyl,N-methacryloylethylammonium bromide (MA-4,16-Br) in monolayers, micells and liposomes was investigated. Kinetics of the polymerization of these surface-active monomers at the interfaces are strongly depend on the position of the polymerizable groups (in hydrophobic or hydrophilic part of the molecules) and on the following conditions (surface pressure, pH, ionic strength,), at which the reactions take place.

Mixed monolayers of these lipid-like monomers with various biologically-active substances (crown-ethers, peptides, enzymes and membrane proteins) were prepared and investigated. It was shown the possibility of the stabilization of special conformations of the peptides and proteins due to the polymerization of the lipid environment or copolymerization of these proteins with lipid matrix.

Kinetics of Collapse and Decollapse of a Single Double-Stranded DNA Chain

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We have found that a single chain of double stranded DNA molecule undergoes first order phase transition between extended coil and compact globule with the addition of various kind of condensation agents, such as PEG^{1,2)}, polyamine³⁾, cationic surfactant⁴⁾, and alcohol. It has become clear that the transition is discrete in a single chain. On the other hand, the transition is continuous as for the ensemble of the DNA chains. Such a fact has been confirmed by the experimental technique of single molecular observation by use of fluorescence microscopy. With fluorescence microscopy, one can evaluate the parameters concerning the size of the coil, such as gyration radius, long axis length, contour length and persistence length, based on the experimental data on the shape of the fluorescent image and also from the Brownian motion. We have observed the time-dependent change of the DNA structure accompanied with the phase transition from coil to globule state. The speed of the compaction is almost constant along the DNA chain. Such a result indicates that the process of the transition is a kind of nucleation and crystal growth in a quasi one-dimensional space. The process of the decollapse of a single DNA has also been observed. The change of the long axis length is described as to be roughly proportional to t^α where $1 < \alpha < 1.5$.

Thus, we have succeeded in the observation of the process of the collapse and decollapse of a single polymer chain. It is expected that the results of the present paper have significant meaning both in polymer physics and molecular biology. The finding that a single DNA chain undergoes the process of nucleation and growth suggests us a clue to solve the long standing unsolved problem; why each chromosome in living cells contains only a single DNA chain avoiding the self- and also inter-chain knotting.

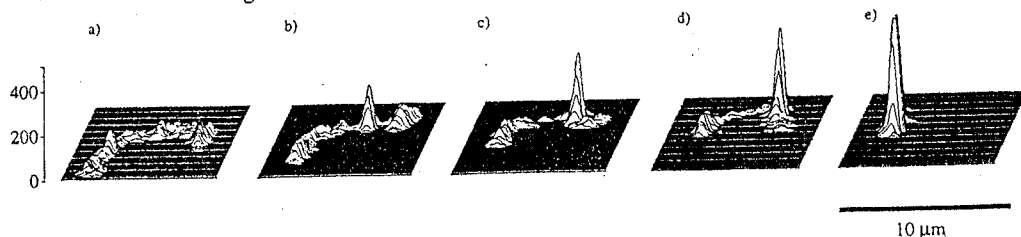


Fig. Time course of collapse of a single T4 DNA molecule(166kbp). The height indicates the intensity of the fluorescent light. The time interval is 2 sec.

[Acknowledgment]

The present paper is a part of the continuing collaboration with Prof. Khokhlov, Dr. Vasilevskaya and the graduate students at Nagoya.

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THE TOPOLOGICAL STRUCTURE OF HYPERSURFACES OF CONFORMATIONAL
ENERGY LEVELS AND PHYSICAL MECHANISMS OF INTERNAL PROTEINS
MOBILITY

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The functionally active biopolymers have interesting and nontrivial dynamic properties. The ideas and concepts concerning protein dynamics undergo evolution with time. Instead of simple models, a type of a Brownian oscillator, a new, more complicated picture arises. In terms of physics, despite the orderly spatial arrangement of atoms, the proteins often behave dynamically as disorderly systems. In this connection, the nonexponential kinetics of chemical processes and non Arrhenius temperature dependencies of the relaxation times are worth of mentioning. Two model approaches have been discussed. First, local diffusion along rough or random potential, and second, the idea of the multiplicity of nonequivalent pathways on a potential energy level hypersurface (ELHS) which a transition can occur from state to state.

The key notion here is conformational energy hypersurface $U(q)$. The points which in the configurational space satisfy Eq. $E=U(q)$ are in conformational energy hypersurface of level E (ELHS).

For instance, in ideal crystals with small energies E ELHS is topologically equivalent to the hypersphere. Another situation is in dynamically disordered systems, for instance, in proteins. The structure of the ELHS is very complicated here even with small energies E . This is because of the availability of degrees of freedom in protein which the potential energy has local maxima, in addition to the minimum. The degrees of freedom of this kind are hydrogen bonds and rotations about single bonds. There are a great many disconnected areas that create conformational substates, which appear as local minima in a one dimensional picture.

A general structure of the ELHS is developed on the basis of Morse's theory. In a three-dimensional projection, the situation can be presented as a set of "octopuses" connected through "tentacles". Such topological structure of ELHS results in a number of consequences for the dynamic behavior of the system and its functioning.

DYNAMICAL COUPLING BETWEEN DNA AND TOPOISOMERASE

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Abstract :

The enzymatic activity of Topoisomerase is necessary in several transformations involving transport of long DNA molecules, such as segregation and condensation during the cell cycle.

We present an in vitro model of the dynamical coupling between Topoisomerase and DNA in a stress field. The balance between two opposite effects is discussed : network formation and removal of stress points. The efficiency of Topoisomerase in the release of topological constraints is related to the Non-Newtonian rheology of the system.

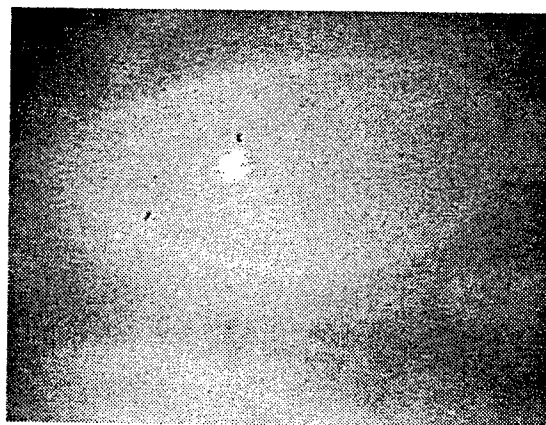
Novel Method to Form Giant Liposome Entrapping DNA

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We found a new method to produce giant liposome with the diameter of several tens micrometers, entrapping DNA molecule within the closed lipid bilayer membrane. The process of the formation of the liposome has been monitored using fluorescence microscopy. Lipid solution (0.1 mg phosphatidyl choline in methanol and chloroform mixture) was situated on a slide glass surface and dried at an ambient temperature. Then aqueous T4DNA (166 kbp) solution (0.6 μ M DNA, 0.6 μ M DAPI and 20 mM $MgCl_2$ in 0.5*TBE buffer) was spread on the glass surface. With this simple procedure, it was found that giant liposomes are formed spontaneously. We have noticed that the presence of magnesium ion is essentially important to produce the giant liposome from phosphatidyl choline. By use of a cationic lipid, dihexadecyldimethylammonium bromide, together with phosphatidyl choline, giant liposome is formed even in the absence of magnesium ion. Interestingly to say, DNA molecules present in the aqueous phase are incorporated into the liposome spontaneously.

Fig.1 exemplifies a liposome entrapping a T4DNA molecule. The DNA molecule inside the giant liposome shows Brownian motion within the closed space, but never escapes from the intra-liposomal space. Thus, we have succeeded in obtaining giant liposome entrapping DNA. It is expected that the novel liposome serves as a model system of living cell. The liposome with DNA may also be useful to realize the effective DNA injection into cells as a new tool for gene therapy.



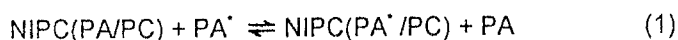
20 μ m

Figure 1. A T4DNA (the bright obstacle in the middle) is entrapped within a giant liposome. DNA is stained with fluorescent dye, DAPI.

Competitive Reactions in Solutions of DNA-containing Polyelectrolyte Complexes

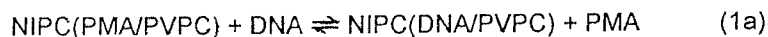
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Water-soluble nonstoichiometric interpolyelectrolyte complexes (NIPCs), being the products of cooperative interaction of polyanion (PA) with polycation (PC), are suitable objects for study of an interpolyelectrolyte reactions, in particular, the interpolyelectrolyte substitution reaction



Polyanions PA^* and PA differ from each other by nature and compete with one another for binding with PC. The model reactions of such a type simulate the charged biopolymers transfer, which determines the regulation of the metabolism and the functioning of the living cell.

We studied for the first time a model substitution reaction with the participation of DNA:



As it follows from ultracentrifugation and luminescence quenching data obtained, DNA-polyanion is able to bind with poly(N-ethyl-4-vinylpyridinium) cation (PVPC) and to substitute poly(methacrylate) anion (PMA) in initial $\text{NIPC}(\text{PMA}/\text{PVPC})$. It was shown that kinetics of reaction 1a was dependent both on PVPC chains D.P. and ionic strength of the solution. The feature of reaction 1a proved to be very slow substitution as compared with a substitution in reaction 1 with the participation of flexible synthetic polyanions PA and PA^* .

The factors of reaction 1a equilibrium control, in particular, the ratio of D.P. of PMA and PVPC chains and the nature of added low-molecular weight electrolyte have been revealed. So, an ability of alkali metal cations to shift the equilibrium to the left was found to be weakened in the series $\text{Li}^+ > \text{K}^+ > \text{Na}^+$ which is in agreement with the cations affinity to native DNA and PMA.

NON-LINEAR EXCITATIONS IN ALPHA-HELIX
AND B-FORM OF DNA-MOLECULE

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Regularity of the structure of above quasi-one-dimensional systems and the following peculiarities in them are taken into account: nearest and third neighbor of polypeptides for alpha-helix, base-base interaction and dissipation for DNA-molecule.

Nonlinear models of the Alpha-Helix given of the S3-type equations [1]; nonlinear models of B-form of DNA given some modified of two sin-Gordons equations [2].

The solutions these equations describe particle-like excitations in alpha-helix "bubble-like" excitations and in DNA kinks, antikinks, and breathers of masses M_s , of energies E_k ,

$E_p(\Omega)$, of momentum $p_s(\nu)$ having a size $l_s(\nu)$ With help of approach [2,3] we have evaluated the contributions of these "particles" on thermodynamic and in dynamic structure factors and discusses of possibility of detection these ones at colorimetric and scattering experiments. The scattering picture of the light and neutron and of the thermodynamics characteristics are modified significantly due to non-linear excitations as well as of pairtype interaction between its excitations.

More detail analyze of infrared spectrum photon and neutron experiments to give possibility to find those particles in real DNA.

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COMPOSITES OBTAINED VIA MATRIX AND PSEUDO-MATRIX PROCESSES (POLYMERIZATION AND NEW PHASE FORMATION)

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A variety of composites comprising nano-structured materials may be created using the processes in which matrix or pseudo-matrix macromolecule effectuate control under formation of another macromolecule ('daughter' chain) or particle of a new phase (the processes in which the macromolecule, after association with freely growing specie, makes the further growth impossible by any reason, are termed pseudo-matrix). The products represent interpolymer (IPC) or polymer - particle (PPC) complexes stabilized with cooperative systems of intermolecular non covalent bonds; composites consisting of IPC (or PPC) and the excess of the matrix or the product of polymerization or condensation of the new phase may be prepared as well.

In comparison with usual way of IPC or PPC preparation (mixing the previously obtained components), matrix and pseudo-matrix processes offer several advantages such as:

- the possibility to prepare IPC, PPC, or composites comprising these complexes, which cannot be obtained by another way;
- control of the size of forming species (e.g., small particles of an inorganic compound) to be included in the final product;
- control of composition and structure of growing on the matrix 'daughter' chains or other species and then control of composition, structure, and properties of the final product;
- the possibility to obtain more perfect successions of intermolecular non covalent bonds between the components of final product (e.g., perfect double-stranded structure of IPC is essential, if the IPC is used as the precursor to obtain ladder polymer by conversion of the non covalent bonds into covalent ones).

Theoretical and experimental data dealing with the influence of different factors on matrix processes (such as mutual molecular recognition of the matrix and growing chains, etc.) on the structure and properties of matrix polymerization products are reviewed.

New experimental data concerning formation of polymer - metal nano-composites comprising highly dispersed metal in course of pseudo-matrix processes, taking place at reduction of metal ions in polymer solutions, as well as matrix polycondensation of tetrahydroxysilica on appropriate macromolecules with formation of IPC of presumably linear polysilica acid and matrix polymer, and several properties of the IPC and respective composites are discussed.

Acknowledgment. The research described in this publication was made possible in part by Grant № 93-03-18096 from the Russian Foundation for Fundamental Investigations and Grant № N2S000 from the International Science Foundation.

ESSENTIALLY NONLINEAR EFFECTS IN STATICS AND
DYNAMICS OF POLYETHYLENE CRYSTAL: ANALYTICAL STUDY
AND NUMERICAL SIMULATION.

N.K.Balabayev, O.V.Gendelman, L.I.Manevitch, M.A.Mazo

The flexibility of the macromolecular chains and strong anisotropy of interactions in the crystalline polyethylene lead to noticeable manifestations of nonlinear phenomena even far from the melting point temperature. The nonlinear effects constitute the reason not only of the conformational transitions but also of different types of twisting, bending and other spatially localized modes, arising due to strong intermolecular anharmonism. These modes may be described as soliton - like solutions of the dynamics equations of PE crystal. They determine such processes as formation of domain walls, dielectric relaxation, plastic deformation, fracture and melting, on the molecular level. Until recently the elementary mechanisms of such processes had been studied on the basis of oversimplified models. In the present research the self - consistent nonlinear dynamics theory of crystalline polyethylene is proposed taking advantage of the asymptotic approach. The corresponding solutions allow us to investigate the structural defects of the system and their mobility. Simultaneously the computer model of PE crystal has been elaborated. It gave an opportunity to study the known types of defects, to compare the results with the analytical theory and to describe some new effects.

CHIRAL CRYSTALLIZATION OF POLYMER CHAINS

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Abstract

Crystallization of achiral or of racemic polymers in chiral space groups appears to be more frequent and relevant than similar occurrences with low-molecular weight compounds. From the crystallization behaviour of some polymers, either racemic or with no intrinsic chirality, showing both chiral and achiral polymorphs, it appears quite likely that formation of chiral crystals is associated with both an energetic and an entropic advantage in the pre-crystallization state, together with the impossibility of interconversion between helices of opposite chirality once the crystal is formed. These features seem to be related with the specific tendency to the close-packed arrangement of approximately cylindrical polymer chains.

General energetic and entropic factors favouring chiral crystallization are discussed. It is shown that the hexagonal arrangement (i.e., the sixfold coordination of helical molecules) in either the crystalline or the pre-crystalline state promote chiral crystallization and is in its own turn favoured by clustering of isochiral helical molecules.

SELF-ASSEMBLY OF DOMAIN WALL OF MOLECULAR TWIST DEFECTS IN POLYETHYLENE CRYSTAL

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Polymer crystals always have structural defects which affect their physical-chemical properties. Theoretical investigations point to a special role of static and dynamical structures which can be described by soliton-like solutions. We carried out numerical experiments on relaxation of polyethylene crystals (PE) structure in both cases when structural defects are absent and when there are defects of molecular twist on 180 degrees.

A calculation cell represented a rectangular parallelepiped with periodical boundary conditions. The cell contained fragments of 96 infinitely-long PE molecules of 150 CH₂-groups for a defectless crystal and 149 units when the crystal had defects of molecule twist on 180 degrees.

Relaxation was studied from two absolutely different initial states of polyethylene sample which had one twist defect on each of its molecules. In the first case the twist defects in the sample initial state formed a domain wall perpendicular to the molecules axis. In the second case the defect on each of the molecules was placed by chance. The relaxation process was conducted by modeling of molecular dynamics at the temperature of 5K and zero outer pressure.

In both cases the polyethylene sample relaxed to one and the same final state. The twist defects arranged as a sloping domain wall at a small angle of 10 degrees to the molecules axes and parallel to one of the crystallographic axes of the PE crystal. The length of the twist region on each of the molecules was 70 units, and the excess potential energy of one defect was 17kJ/mol.

Side-Chain Crystallization of Amorphous Polymers due to Self-assembling induced by CT-Interaction

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It has been shown that charge-transfer interaction between polymers containing (depending on the nature of the polymers) a critical minimum number of electron-donor and electron-acceptor side-groups, respectively, leads to an increased elasticity due to thermoreversible network formation. CT-interaction can also be used for compatibilization and phase-stabilization in incompatible polymer blends. It has been shown that the thermoreversible network formation is also effective in blends of low-molecular bi-interacting donor-carbazoles with polymeric acceptors, but not in blends of polydonors with low-molecular mono-acceptors.

The attempt of using low-molecular, rod-like bi-acceptors in connection with amorphous, methacrylic side-group polydonors resulted in the self-assembling of the side-groups due to CT-interaction. The side-group self-assembling is accompanied by a side-chain crystallization of the amorphous polymers, provided the given spacer-length disconnects the donor side-group from the polymeric backbone.

The crystallization was evidenced by optical microscopy, DSC and WAXS, the latter confirming unequivocally the new crystalline structure shown by the self-assembled 1:1 D/A blend, quite different from the crystalline structure of the low-molecular biacceptor. Comparative molecular simulation of the most probable conformations of respective 10 repeating units of the amorphous polydonor and of the D/A blend indicates an extension of the polymeric backbone in the blend, expressed by a substantial increase of the end-to-end distance. In the same time a tendency of helicoidal arrangement and stacking of the side-chain CT-complexes is suggested. Additionally, DSC-measurements point in the heating scans by the intermediate endothermic first order peak before the melting peak at a possible formation of LC-mesophases, as observed by Ringsdorf et al. in similar systems. The formation of intermediate LC-phases seems mainly valid for blends of the low-molecular bi-acceptor with siloxanic polydonors.

THE SINGULARITIES REGIONS IN SEMI-CRYSTALLINE POLYMERS

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Semi-crystalline polymers can be considered as the typical polycrystalline solids. It is widely known that the real properties of solids depend on the structure of interfacial regions between structural units at the great extent. In polymers, a whole hierarchy of the structural units exists. More complicated supermolecular structures (spherulites and stacks) are formed from elementary lamellae and microfibrils. The boundaries between polymer structural units appeared to have an outstanding distinction from those in the conventional solids. Essentially, the one and the same macromolecule can be incorporated into several ordered (lamellar crystalline core) and disordered (interlamellar) regions. The latter include the portions of molecules in a shape of regular folds, those of different degree of coiling (loose loops) and tie molecules. The use of NMR, WAXS and SAXS techniques allows to determine the content of all above mentioned components. IR-spectroscopy evidences that the conformational structure of macromolecules in disordered regions differs dramatically from that in a statistical coil, which is associated with a concept of amorphous phase. As a consequence of the peculiar features, the thickness of interfacial boundaries in polymers is larger by 1–2 order of magnitude than that in the conventional solids and reach tens or even hundreds of Å. The specific interfacial structure of interlamellar regions controls not only relaxation; properties of semi-crystalline polymers in comparison to entirely amorphous ones but also influences significantly on both internal structure of crystalline regions (large offending pre-surface zones, peculiar change in the crystalline sizes under the of external actions ... etc.) and on the thermodynamic characteristics derived from the study of melting process by DSC. The analysis of all the data obtained enables one to draw a conclusion that widely used a two-phase model developed for interpretation structure/property relationships is not enough correct.

An experiment to study Polymer structure development under pressure and at high cooling rates.

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Polymer solidification under usual processing conditions is a complex phenomenon in which the kinematics of flow, high thermal gradients and high pressures determine the structure formed.

The study of polymer structure formed under pressure is thus of industrial and scientific interest but to date has only been studied using conventional techniques such as dilatometry and differential scanning calorimetry. The experiments possible using such equipment are either isothermal or non isothermal but at cooling rates several orders of magnitude than those experienced in industrial processes. A new apparatus has been developed to study the crystallisation of polypropylene when subjected to pressure and cooled rapidly. The experimental methodology of following the thermal history of rapidly cooled samples and then analysing the resulting sample morphology, as recently applied to rapid cooling experiments under atmospheric pressure⁽¹⁾, has been utilised to study the effects of rapid cooling experiments under pressure.

An injection mould has been designed such that polymer is fed, under a set pressure, into a mould chamber closed by a thermally conductive diaphragm. Coolant is then sprayed onto the other side of the diaphragm such that the sample is cooled at a known cooling rate and under a known pressure. Polarised microscopy (POM), x-ray diffraction (WAXD) and density measurements are then used to characterise the sample morphology.

Results of density vs. depth for individual samples produced from an iPP grade supplied by Himont, show a density gradient increasing with depth into the sample. For different cooling rates a density plateau is reached at a depth from the surface of around 2 mm. As shown in figure 1, the initial density gradient within the samples is low thus a consistent morphology is created until a depth of around 300 μm allowing subsequent morphological analysis to be conducted and directly related to the recorded cooling velocity and pressure. These effects were also confirmed visually using POM techniques as the observed change of size of spherulitic dimensions on fast and slow cooled samples is initial small, increasing rapidly until a more or less constant size and distribution is reached at around 2 mm.

Morphological characterisation of samples rapidly cooled at low pressure show a predominant alpha phase structure up until a cooling velocity of around 60 $^{\circ}\text{C}/\text{sec}$, where upon a rapid phase transition to the 'smetic' or 'condis crystal' state is observed for increasing cooling rates, by a significant drop in density, figure 2. These results have been verified and quantified, in terms of phase content, using WAXD and a deconvolution process. The preliminary results of rapid cooling experiments under pressure are compared to the results of rapid cooling experiments for the same iPP grade under atmospheric pressure in figure 2. The main feature displayed by these results is a lower density and a lower density dependence on cooling rate, for increasing pressure. These results possibly open new doors in the determination of polymer solidification behaviour, but need further conclusive verification.

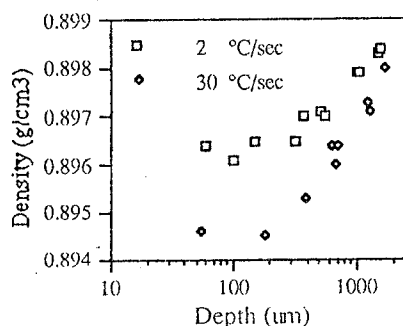


Fig 1. Density vs. Depth.

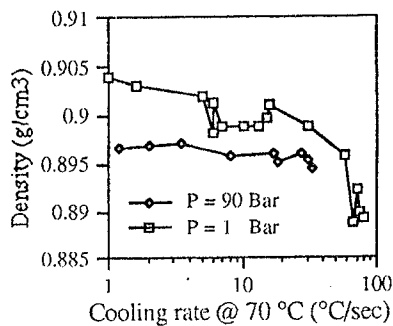


Fig2. Density vs. Cooling rate.

Ref :1) S. Piccarolo, M. Saiu, V. Brucato, G. Titomanlio, *J. App. Poly. Sci.*, 46, 625, (1992)

SIMULATION OF ELASTIC AND SUPERELASTIC BEHAVIOR OF DISORDERED CONTINUA

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Abstract: Computer simulations on the wide and long strips are performed with a goal to obtain elastic and superelastic threshold, p_e , and exponents, T and S . Finite size scaling is used. Finite element based micromechanical model is the distinctive feature of the present approach. The way of approximation makes the model close to the site percolation problem. The values $p_e \approx 0.48$, $T/\nu \approx 1$, $S/\nu \approx 1$ found are close to the data of the recent simulations on discrete lattices made in frameworks of central-force interaction between randomly disposed sites (Ref. 1). Unexpected extreme-type change of Poisson ratios with the increase of rigid component fraction is discovered.

COMPUTER SIMULATIONS ON NOVOLAK-PHENOL FORMALDEHYDE RESIN

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Amorphous ensembles of phenol formaldehyde resins were created at the experimentally given density and molecular dynamics calculations were carried out at various temperatures. The role of hydrogen bonds within the material is illustrated by determination of the radial distribution function and IR frequencies obtained from local mode analysis. These results are compared with experimental IR measurements at different temperatures. Additionally, the simulated X-ray pattern will be presented.

ON THE MECHANISM OF PLASTIC DEFORMATION OF SIMPLE AND POLYMERIC GLASSES.

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The model describing the mechanism of plastic deformation in disordered solids is introduced on the basis of the concept taking advantage of the point - like structural defects. These defects are supposed to be responsible for both the mechanical behavior and abnormal thermal properties which are peculiar for the majority of known glassy systems. This supposition may be supported by the consideration of the character of localization of low - frequency vibrational modes connected with such defects. The approach regarded gives also an opportunity to estimate the parameters of structural defects.

On the basis of the concept developed it turns out to be possible to describe the process of plastic deformation as the subsequent appearance of new defects and to predict the value of the yield stress. The consideration of the interaction between the defects gives an opportunity to reveal the structures formed by appearing defects (shear bands).

For the case of polymer glass the problem concerning the description of the core of defect may be simplified essentially if taking into account the characteristic hierarchy of interactions. It is possible to construct appropriate model and to predict the characteristics of plasticity in satisfactory accordance with the experimental data.

THE SPECIFIC FEATURES OF CONFORMATIONAL BEHAVIOR OF PHYSIOLOGICALLY ACTIVE POLYMERS

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Some features of conformational behavior of flexible-chain and rigid-chain polymers modified by protein molecules have been studied. It was shown that immobilization of proteins on flexible-chain polymers results in a marked change their conformation in solution. Despite of the random distribution of protein molecules along the polymer chain the coil of the polymer undergoes substantial contraction due to the flexibility of the backbone and the inherent tendency of protein molecules to associate. The greater is the flexibility the more compact the macromolecular structure is. The increase of the chain rigidity neutralizes the perturbing effect of the protein, prevents the aggregation of the protein molecules, and thus alleviates their interaction with substrate.

A new approach to the targeted thermally activated transport of physiologically active compounds was proposed. The approach involves the immobilization of these compounds on preliminary activated poly-N-alkyl-substituted acrylamides showing lower critical solution temperature and heating the delivery site above this temperature. The approach was illustrated with trypsin and horseradish peroxidase immobilized on N-isopropyl-acrylamide-acrylamide-N-acryloylphthalimide ternary copolymers. It was shown that immobilization of enzymes on these copolymers would not lead to loss of enzymatic activity if the enzymes were not sensitive to hydrophobic interactions.

DISCRETE COIL-GLOBULE TRANSITION OF SINGLE LARGE DNA MOLECULES INDUCED BY CATIONIC SURFACTANT

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The conformational dynamics of the T4DNA molecules in aqueous solution in the presence of cationic surfactant, cetyltrimethylammonium bromide (CTAB) was studied. We have found that large DNA molecules exhibit discrete conformational change between coil and globule states with the addition of very small amount (with the order of 10^{-5} M) of CTAB. We used the fluorescence microscopy as a tool of single molecular observation of double-stranded T4DNA in an aqueous environment. When the concentration of CTAB was less than $9.4 \cdot 10^{-6}$ M, all DNA molecules exhibited extended coil state. Whereas, when the CTAB concentration was higher than $2.0 \cdot 10^{-5}$ M, only compacted DNA molecules in globular state were observed (Fig.1). In the region between these two critical concentrations, the coil and globule states coexisted in the solution. Small but apparent increase of the size of DNA globule was noticed at the CTAB concentration higher than 10^{-3} M, due to the penetration of CTAB molecules into the DNA globule. To study the dynamical aspect of coil-globule transition, the process of the structural change from coil into globule state was observed under the spatial gradient of the CTAB concentration. The formation of aggregates from two or more globules was noticed at high concentrations of surfactant above $1.6 \cdot 10^{-4}$ M.

Translational diffusion constant D of DNA molecules was measured from the time-series of video frames of the fluorescence image. Hydrodynamic gyration radius ξ_{II} was evaluated from the D and the viscosity of the bulk aqueous solutions. The increase of the globule size at the higher CTAB concentrations above 10^{-3} M was confirmed by the increase of ξ_{II} values.

Potentiometric titration with the use of ion-selective membrane was applied to estimate the binding degree of CTAB to T4DNA. The resulting binding isotherms (Fig.2) were compared with the results obtained by the fluorescence microscopy. The reverse transition of single DNA molecule from coil into globule state was also observed by fluorescence microscopy.

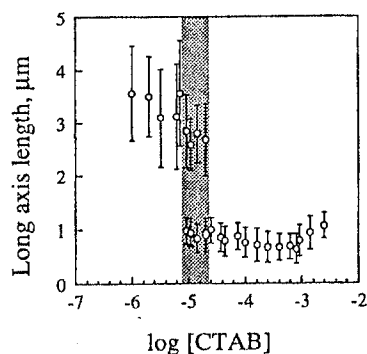


Figure 1. Long axis lengths of T4DNA molecules vs logarithm of CTAB concentration (the opened circles indicate maximums of the DNA lengths' distribution). Statistical error in the distribution is given as the standard deviation.

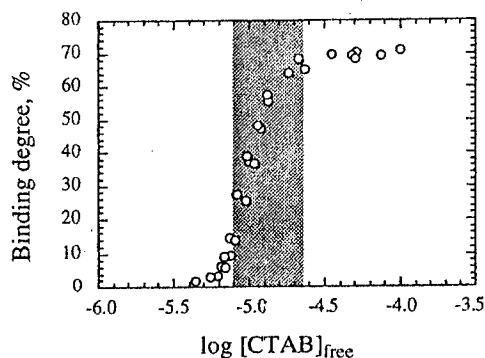


Figure 2. Binding isotherm of CTAB-T4DNA system at 20°C. The shaded region corresponds to that in Figure 1.

Acknowledgment

We would like to acknowledge Dr. Yukiko Matsuzawa (Nagoya University) and Prof. Noriyuki Kumazawa (Ibaraki University) for the technical assistance.

Collapsed Single DNA Chain Memorizes the Past in its Higher Order Structure

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From the single molecular observation of giant DNA by use of fluorescence microscopy, higher order structure of the complex between DNA and cationic polypeptide, poly-arginine(p-Arg), was studied in dilute aqueous solution. In this condition, single molecular compaction of DNA is induced. It was found that the steric size of the complex gradually decreases with the increase of the concentration of p-Arg. In addition to this result, we have noticed that the higher order structure of the complex exhibits interesting characteristics, i.e., the condensed structure memorizes the history of the sample preparation. The size distribution of the condensed structure of the complex showed a marked difference depending on the time-course of the addition of p-Arg and NaCl to the DNA solution.(Fig.)

The present results suggest that the condensed structure of DNA has many stationary states with free energy minimum, and that kinetic effect becomes essential to determine the structure among the multi-steady states. Actually, if we take into account the kinetic effect of competitive interaction of p-Arg and Na^+ ion with a single DNA molecule, it is explained that the steric size of the complex exhibits multistability.

The multistability is expected to be deeply concerned with the self-regulation of the condensed structure of DNA and with the dynamical process of gene expression in living cells.

Reference:Minagawa, K., Matsuzawa, Y., Yoshikawa, K., Khokhlov, A. R. and Doi, M.(1994) *Biopolymers* 34, 555.

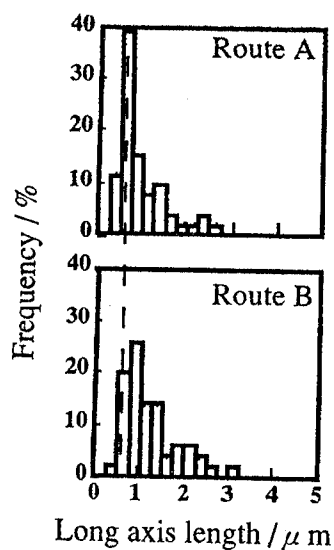


Fig. Distributions of long axis length of the complex formed in route A and B. In route A, p-Arg was added as first to the DNA solution, and then NaCl was added. In route B, inverse procedure. The long axis length is defined as the longest distance in the outline of the video image of the complex.

ASSOCIATION AND SOLVATION IN THE PROCESS OF DISSOLUTION OF POLY(ACRYLIC ACID) IN WATER AND NON-AQUEOUS SOLVENTS.

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Solubility of poly(acrylic acid) (PAA) in a broad variety of solvents with different electron donor-acceptor properties was studied in 270-450 K temperature range. Only those able to provide strong specific interactions were found to dissolve PAA. Interactions of PAA and poly(methacrylic acid) (PMA) with water and non-aqueous solvents were studied by means of Tian-Calvet calorimetry. Excess enthalpies of solution and partial excess enthalpies of solvent and polymer were determined along the entire composition range at the temperatures of 290-305 K for the systems PAA-water, PAA-butanole, PAA-DMFA and PMA-water.

Curves of partial excess enthalpies vs composition for aqueous solutions of PAA showed specific features never observed for any of polymer-solvent systems studied earlier. First, interaction between PAA and water appeared to be quite poor compared to that in butanole and DMFA and second, multiple peaks vanishing with temperature increase were found out on partial excess enthalpy curves in concentrated solutions. While weight fraction of PAA in aqueous solution was about 0.6-0.7, initially poor interaction of its segments with water molecules abruptly improved. Neither in aqueous PMA solutions nor in non-aqueous PAA solutions anything similar was observed. This was taken as an indication of specific features of PAA structure and its changing in the process of dissolution in water.

It might be assumed that the structure of solid PAA is formed of dense associates due to intermolecular H-bonds. As water is the solvent nearly unable to take part in Van-der-Waals forces and thus failing to interact with hydrocarbon chain, these associates remain in concentrated solutions while water content is comparatively low. When number of water molecules in the system reaches certain value high enough to break intermolecular H-bonds altogether, these associates are destroyed cooperatively in rather narrow composition range and PAA solvates are formed. None of these occur in PMA solutions because dense association is suppressed by steric effect of methyl group or in non-aqueous PAA solutions because of high extent of Van-der-Waals forces there.

Static and Dynamic Light Scattering measurements on dilute solutions of Methylcellulose as a function of temperature.

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Methylcellulose (MC) is a self associating polysaccharide hydrosoluble at low temperature and forming, in semi-dilute regime, a thermoreversible gel upon heating.

Until now, the structures and processes involved in the thermogelation of MC solutions are not well established. In order to clarify the molecular mechanism of gel formation, we have first studied the behaviour of MC in dilute solutions ($c < c^*$) using light scattering.

Static and dynamic light scattering measurements have been performed on solutions of commercial samples (Methocel from the Dow Chemical Compagny) and of few other MC synthesized in our laboratory. The properties of these aqueous solutions of MC have been studied as a function of temperature (from 20 to 60°C).

The molecular weight, radius of gyration and second virial coefficient were obtained from the static scattering data. We found that the molecular weight \bar{M}_w remained constant while increasing the temperature from 20 to 50°C.

Scattering of light through the samples began to increase strongly from 55-60°C characterizing the ability of the polymer to aggregate. Moreover, a kinetic process was underlined at these temperatures.

Dynamic light scattering data indicated that, at the lowest temperatures, one distribution of molecules is present in solution (the correlation function exhibited a single relaxation); whereas at 60°C a second one ('slow mode') appears clearly corresponding to a formation of aggregates.

These results were confirmed by GPC experiments showing a starting of aggregation above 50°C.

Additionally, the effect of the degree of substitution (\bar{DS}) on the conformation of the molecules during heating was studied. Preliminary results obtained with rheological experiments showed different behaviours according to low or high \bar{DS} values.

INFLUENCE OF SALTING-IN EFFECTS ON THE PROPERTIES AND STABILITY OF HYDROGEN-BONDED INTERPOLYMER COMPLEXES

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It is well-established that neutral salts can exert a pronounced effect on the structure and conformational stability of single macromolecular species in aqueous solution, leading to either an increase or decrease in solubility. These solubility changes are referred to as "salting-in" and "salting-out," respectively. Similar effects are expected when salts are added to hydrogen-bonded interpolymer complexes (IPCs), which constitute an interesting class of macromolecular systems. In this work, polyacrylic acid (PAA) and polymethacrylic acid (PMAA) have been employed as proton acceptors, while polyethylene oxide (PEO) and hydroxypropylcellulose (HPC) have been utilized as proton donors to form a series of novel IPCs. The presence of PMAA and HPC in these IPCs is particularly interesting, since they impart additional stabilization due to hydrophobic interactions. In addition to the pure IPC systems, solutions containing salts which induce either "salting-out" (e.g., NaCl) or "salting-in" (e.g., NaSCN) have been examined here by viscometry, potentiometry and turbidity measurements, as well as by freeze-fracture transmission electron microscopy. It will be shown that "salting-in" results in IPC properties comparable to those obtained through addition of an organic solvent, including full complex dissociation. Based upon these observations, a mechanism addressing the influence of salts on IPC properties and conformations will be described.

BLOCK COPOLYMER GELS: A NEW FAMILY OF THERMOTROPIC THIXOTROPES

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Addition of a self-associating agent, such as dibenzylidene sorbitol (DBS), to a number of homopolymers results in the formation of either nucleated crystals (if the polymer is semi-crystalline), dispersed aggregates (if no interactions with polymer occur) or thermoreversible physical gels (if the polymer hydrogen-bonds with the agent). In this work, we have explored the morphological and thermo-mechanical properties of a series of gels formed by small quantities of DBS (typically less than 2 wt%) and amphiphilic graft and block copolymers composed of dimethylsiloxane, ethylene oxide and propylene oxide segments. These copolymers are structurally disordered, behaving as viscous liquids. Morphological studies of these gels have been possible through the use of supercritical fluid extraction in Freon 13. Field-emission scanning electron micrographs of polymer-extracted gels reveal the presence of an intact, highly interconnected percolation network comprised of DBS fibrils measuring 10-20 nm in diameter. The morphology of this network can be readily altered by changing the composition or molecular architecture of the copolymer matrix. In addition, some of these gels exhibit a hierarchical structure, as discerned by correlated optical/electron microscopy and dynamic strain rheology. Rheological measurements obtained with a dynamic stress rheometer will also be presented and will demonstrate that these thermotropic gels exhibit thixotropic properties.

FLORY TYPE THEORY FOR SWELLING AND COLLAPSE OF A KNOT

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It is well known that the equilibrium knotting of the phantom ring is suppressed by swelling and facilitated by collapse. Accordingly, we expect the size of real non-phantom ring to depend strongly on the amount of knots "quenched" in the ring during its preparation. Furthermore, at any given amount, knots will resist either swelling in a good solvent or collapse in a poor solvent, because chain goes to the state for which it is either "overknotted" or "underknotted."

To describe the effect, we trade even slightest attempt of mathematical sophistication for the solvability and suggest the following Flory-type theory. Suppose we have a polymer with a given amount of knots. Let us take a tube of some diameter d and make it knotted topologically equivalent to the given state of our polymer. Let us take the shortest length of the tube, L , which can make the required knot (with the given diameter d). In this case, the tube occupies essentially all the space in the knot, so that characteristic size of the structure R is given by $R^3 \sim Ld^2$. Clearly, the ratio $p = L/d$ does not depend on either d or L , but on the knot topology. We employ p as the topological invariant and call it "primitive path" (it is similar to what is known by this name in other topological models). We now represent our knotted non-phantom polymer as phantom ring confined within the given knotted tube. Unknotted polymer is characterized with $p \sim 1$, and $p \gg 1$ corresponds to heavily knotted polymer.

In terms of this model and using standard notations, we go on to write the free energy

$$F = F_{el} + F_{int}; \quad F_{el} = \frac{L^2}{Na^2} + \frac{Na^2}{d^2}; \quad F_{int} = \frac{BN^2}{R^3} + \frac{CN^3}{R^6} \quad \left[\text{with } R^3 = Ld^2 \text{ and } p = \frac{L}{d} \right].$$

The elastic term is due to the confinement in the tube, where polymer "does not know" whether the tube is knotted or not in the embedding space. This yields the results: $R \sim N^{1/2}p^{-1/6}$ for ideal polymer ($B = C = 0$), meaning that the chain is getting more compact while more knotted (growing p); θ regime (with $R = R_{id}$) takes place when $-B \sim (C/a^3)\sqrt{p/N}$, which is getting down into the poor solvent with growing amount of knots; in a good solvent, $R \sim aN^{3/5}p^{-4/15}$ - the scaling of N dependence is not changed, but knotted chain is generally more compact; $R \sim aN^{1/3}$ in the dense globule, where R is dictated by packing and cannot be altered.

Dynamics, properties of linear polymer, and comparison to simulation data will be discussed.

POLYMER-SURFACTANT COMPLEXATION IN AQUEOUS SOLUTIONS OF
HYDROFOBICALLY MODIFIED POLYCATIONS AND VESICLES OF VARIOUS
SURFACTANTS.

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Interactions between vesicles based on cationic or betain type of synthetic lipids, i.e. didodecyldimethylammonium bromide (DDAB) or dilauroyl phosphatidilcholine (DLPS) with amphiphilic polycations are studied using turbidimetry and ultracentrifugation (sedimentation velocity mode) techniques. Amphiphilic polycations were copolymers with N-ethyl-4-vinylpyridinium bromide monomeric units and small amounts (up to 10-18 molar %) of either N-dodecyl-4-vinylpyridinium bromide or N-cetyl-4-vinylpyridinium bromide monomeric units. Poly(N-ethyl-4-vinylpyridinium bromide), (PEVP), was used as the reference polycation.

Amphiphilic polycations which underwent conformational transition and are in compact conformation due to predominant intrachain association of hydrophobic chain units in the dilute solutions efficiently disrupt both DDAB and DLPS vesicles. A complete disruption of vesicles results in the formation of copolymer-surfactant complexes with the composition of 1-2 surfactant molecules per copolymer hydrophobic chain unit.

Copolymers with relatively small amounts of hydrophobic chain units, which do not form hydrophobic intrachain associates, do not disrupt DDAB vesicles, though completely disrupt DLPS vesicles with the formation of polycation-surfactant complexes having the composition of 1 surfactant molecule per 2-3 hydrophobic chain units of the copolymer.

Note, that PEVP does not interact with DDAB vesicles, while PEVP adsorbs on the DLPS vesicles and cause some changes in their aggregation state.

One can suggest that hydrophobic interactions are playing the decisive role in the disruption of the studied vesicles and the formation of the copolymer-surfactant complexes. The observed difference in the behavior of vesicles formed by cationic or betain type of lipids may be attributed to the additional electrostatic contribution to the copolymer-vesicles interaction, which may facilitate adsorption of amphiphilic polycation on DLPS vesicles and the following disruption of such vesicles.

NEW NONSTOICHIOMETRIC (POLYELECTROLYTE-SURFACTANT) COMPLEXES
SOLUBLE IN LOW-POLARITY SOLVENTS.

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We have found recently that stoichiometric complexes (SPC) composed of a linear synthetic polyelectrolyte and simple low-mass surfactants of an opposite charge can be dissolved as individual compounds in some low-polarity organic liquids [1]. We have developed an approach to synthesize new nonstoichiometric complexes (NPC) of polyelectrolytes and oppositely charged surfactants, based on an exchange reaction of low-mass counterions between SPC and free polyelectrolyte chains in the mixed organic solvent [2]. Such NPCs have "excessive" polyelectrolyte chain units (normally 10-30 molar percent on average) in which surfactant ions are substituted for simple low-mass counterions. A systematic study of solubility and conformational state of both SPC and NPC in low-polarity solvents is undertaken in the present contribution on the example of complexes of poly(N-ethyl-4-vinylpyridinium bromide) and sodium dodecylsulfate. The molar percent of "excessive" polyelectrolyte chain units (ϕ) is used below to designate composition of the NPCs. It was shown that SPC and NPCs of various ϕ dissolve in chloroform, and neither interchain aggregation nor dissociation into individual components is observed in dilute solutions of such complexes. A pronounced compaction in dilute solutions of the studied complexes in chloroform is found while passing from SPC to NPCs with the increased ϕ value. Solubility of SPC, NPCs decreases abruptly in the order of chloroform>chlorobenzene>benzene and with the decrease in ϕ . A dominating interchain aggregation is observed for SPC, NPCs in dilute solutions in chlorobenzene. An introduction of one volume percent of cosolvent (methanol) to SPC, NPCs dilute solutions in chloroform and chlorobenzene:

- does not cause any change in diffusion coefficient (D_m) of the SPC in chloroform;
- cause an increase in D_m of the NPCs in chloroform up to the value characteristic of the SPC;
- cause an increase (more then an order of magnitude) in D_m of SPC, NPCs in chlorobenzene up to the values close to those of complexes in chloroform.

The studied NPCs represent new "ionomers" in which excessive polyelectrolyte chain units are playing the role of "ionogenic groups" with the pronounced tendency to aggregate in low-polarity solvents and in the bulk. A peculiarity of such "ionomers" is the possibility to form self-organized structures due to interaction of surfactant hadrocarbon radicals, migration and segregation of surfactant ions in NPC particles.

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HYDRODYNAMICAL, DYNAMO- AND ELECTROOPTICAL CHARACTERISTICS OF IONOMER - SURFACTANT COMPLEXES IN NONPOLAR SOLVENT

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Hydrodynamical, dynamo- (flow birefringence) and electrooptical (Kerr effect) characteristics of sulfonated polystyrene ionomers, containing 1,35 molar percent of $-SO_3Na$ salt groups (SPNa), sodium bis-(2-ethylhexyl) sulfosuccinate (aerosol OT or AOT) molecules and complexes of SPNa+AOT ($[SPNa]/[AOT] = 2,5$ in monomer moles) in nonpolar organic solvent m-xylene were studied.

Dependences of sedimentation (S) and diffusion (D) coefficients, reduced viscosity (η_{red}), electric birefringence (EB) and relaxation times (rotational diffusion coefficient) on solutions concentration C were investigated.

A nonlinear changes of S and D values as well as a big value of EB and nonexponential rise and decay of EB confirms the existing of intermolecular aggregation in solutions of SPNa ($C > 0,2$ g/dl), AOT ($C > 0,2$ g/dl) and SPNa+AOT ($C > 0,5$ g/dl). From translation diffusion and viscosity data in dilute solutions of SPNa ($C < 0,2$ g/dl) the decreasing of single coils dimensions as compared with that of polystyrene (PS) coils with the same degree of polymerization in m-xylene was founded. That is caused by the intramolecular interaction between ionomer salt groups. In the presence of AOT molecules the reduced viscosity (for $C < 0,47$ g/dl) and diffusion coefficient D (for $C < 0,1$ g/dl) in SPNa+AOT solutions are near to η_{red} and D of PS. Analysis of translation diffusion, sedimentation and EB data shows that the part of AOT molecules are associated with SPNa salt groups and, consequently, forms ionomer-surfactant complexes in nonpolar solvent.

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SELF-ASSEMBLY IN AQUEOUS SOLUTIONS OF AMPHIPHILIC POLYCATIONS AND SURFACTANTS OF THE SAME CHARGE.

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A systematic study of complexation of hydrophobically modified amphiphilic polycations based on quaternized poly(4-vinylpyridine) bearing 10-20 molar percent of dodecyl or cetyl hydrophobic groups with surfactants of the same charge is carried out in aqueous solutions. It is shown, that in spite of electrostatic repulsion of the partners the formation of amphiphilic polycation-surfactant complexes occurs due to hydrophobic interactions in dilute aqueous solutions. The complexation of amphiphilic polycations and surfactants of the same charge proceeds differently in two regions of copolymer:surfactant concentration ratio. At surfactant concentrations in the mixture lower or equal to the surfactant CMC, the formation of joint aggregates of several hydrophobic chain units of the copolymer and surfactant molecules takes place. Such aggregates are playing the role of "crosslinks", causing compaction of the copolymer coils in dilute solutions. The average composition of the complexes thus formed is about 1-6 surfactant molecules per one hydrophobic chain unit of the copolymer and is shown to depend on hydrophobic-lipophilic balance of the partners and the initial conformational state of the amphiphilic polycation. At the surfactant concentrations in the mixture exceeding the CMC, disruption of intrachain aggregates occurs leading to "unfastening" and expansion of the copolymer coils. The individual hydrophobic chain units play the role of molecular "anchors", binding surfactant with the formation of joint micelles, as has been shown previously for analogous complexation in low-polarity solvents [1-3].

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A STUDY OF CATION AND ANION EFFECTS ON THE STABILITY AND BEHAVIOR OF WATER-SOLUBLE INTERPOLYELECTROLYTE COMPLEXES.

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Water-soluble interpolyelectrolyte complexes (IPEC), being the products of an interaction between opposite in charge polyelectrolytes taken in non-equivalent ratios, are very important in many industrial applications and also as simplified and suitable models of self-assembling supramolecular complexes of charged biopolymers. The properties of IPEC are well known to be drastically affected by ionic strength of their solutions. In this paper, we have shown that the chemical nature of small ions is a great influence on the stability and behavior of IPEC formed by lyophilizing poly(methacrylate) anion (PA) and blocking poly(N-ethyl-4-vinylpyridinium) cation (PC).

According to the ability to induce the IPEC complete dissociation, monovalent ions were found to exhibit the following orders: $\text{Br}^- > \text{Cl}^- > \text{F}^-$ and $\text{Li}^+ \geq \text{Na}^+ > \text{K}^+ > (\text{CH}_3)_4\text{N}^+$. Both orders appear to be in a good agreement with the affinities of these cations and anions to PA and PC, respectively.

The chemical nature of small ions was also found to determine the behavior and properties of IPEC in dilute water-salt solutions. As it follows from obtained phase separation diagrams, an addition of tetramethylammonium halides to IPEC solutions does not cause their phase separation. Such behavior is in contrast to that observed for alkali metal chlorides, an injection of which in IPEC solutions usually leads to their phase separation. This distinction is thought to be due to differences in relative binding strengths of cations and anions to corresponding IPEC components in these two cases. In solutions of alkali metal chlorides, the effect of cations, which bind with lyophilizing PA decreasing the hydrophilicity of IPEC, is likely to determine the behavior of IPEC. However, the effect of anions, which bind with blocking PC increasing the hydrophilicity of IPEC, is probably responsible for properties of IPEC in solutions of tetramethylammonium halides.

The possible conformational changes of both IPEC components that result from binding of small ions with their groups have been considered.

HYDRODYNAMICAL, DYNAMO- AND ELECTROOPTICAL PROPERTIES OF POLYELECTROLYTE-SURFACTANT COMPLEXES IN CHLOROFORM.

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Physico-chemical properties of polyelectrolyte complexes are the subject of active scientific research at last years. Recently, a new polymer complexes (PC) of poly-N-ethyl-4- vinylpyridiniumcation, Br(-) and dodecylsulfate (DS(-)) anions soluble in some low-polar organic solvents were synthesised in our laboratory.

The results of hydrodynamical, dynamo- and electrooptical studies of PC with different number fraction of DS(-) anions f in macromolecules are discussed in this report. For all investigated samples, the influence of polyelectrolyte effects on translation diffusion and viscosity has been not displayed. Intrinsic viscosity $[\eta]$, diffusion and optical shear $dn/d\Gamma$ coefficients, Kerr constant dependences on f have been observed. The estimation of thermodynamical rigidity from viscosity and flow birefringence data showed that Kuhn segment length A of PC changes from 2.7 nm to 5.4 nm with variation of composition f from 0.55 to 1, besides flexibility $1/A$ linearly depends on f . The segment length A has a value order the same as A of some comblike flexible-chain polymers and copolymers. It's alteration with the PC composition just as it takes place in ordinary comblike statistical copolymers. Moreover, the change of PC coils dimensions with variation of f is caused by the interaction of ionogenic groups, containing Br(-) anions. The orientation of PC molecules in electric field is caused by induced dipole moment, relaxation time of which is close to the relaxation time of macromolecular orientation. The dependence of Kerr constant on PC composition and polymerization degree is caused by the changing of optical anisotropy and deformation polyrizability of macromolecules.

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NON-SPHERICAL MICELLES IN SOLUTIONS OF POLYMERS WITH STRONGLY INTERACTING GROUPS: COMPUTER SIMULATIONS

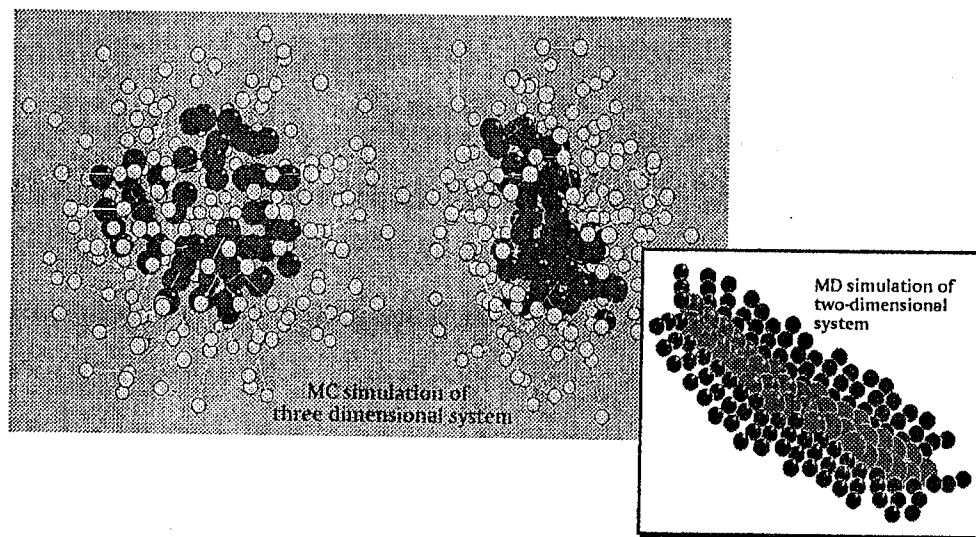
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In recent years, an intensive attention has been paid to polymeric systems with strongly interacting groups, i.e., polymers containing ionic groups which strongly attract each other.

Using highly idealized 2- and 3-dimensional models we have performed Monte Carlo lattice and molecular dynamics off-lattice computer simulations of these systems in the so-called *superstrong segregation limit*. In particular, micellar cluster formation in solutions of regular ionomers with extremely short attractive "head" blocks ($N_a=1$) and repulsive flexible-chain "tail" blocks of N_b links is studied. The interaction between "head" A-blocks is described by screened electrostatic potential. Starting at infinite temperature to randomize the molecular configuration, the systems are slowly "cooled", and microstructures spontaneously self-assemble at low temperatures. The simulation technique is used to study a wide variety of interesting phenomena, from micelle size and shape transitions to packing transitions and phase behavior to interfacial properties. In particular, it is shown that as the effective energy of attraction between A-blocks becomes much larger than $k_B T$ the most stable shape of micelles changes from spherical to *disk-like* (in three dimensions) or *lamellar* (in two dimensions). Typical examples of the non-spherical micelles are presented below.



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EFFECT OF SURFACTANTS ON THE SWELLING BEHAVIOR OF THE POLYAMPHOLYTE GELS

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The present study deals with the high-charged-density polyampholyte networks formed from sodium methacrylate and diallyldimethylammonium bromide. Polyampholyte gels were synthesized in fresh water and in presence of NaBr to prepared the networks with different microstructure. The monomer compositions were varied. The swelling behavior of polyampholyte gels as the function of their compositions was determined. It was shown that the swelling of the gels in water is strongly dependent on the electrostatic interactions and molecular structure of the network. The polyampholyte gels with balanced stoichiometry show minimal swelling.

The present study is mainly focused on the interaction of the polyampholyte gels with ionic surfactants (cetylpyridinium chloride and sodium dodecylbenzenesulfonate). The balance between cationic and anionic units of the polymer chains defines the swelling behavior of the polyampholyte gel in the surfactant solution. It was shown that for the polyampholyte gels with an excess of the charges of one sing the addition of oppositely charged surfactant leads to the collapse of the gel. The swelling of polyampholyte gels in the isoelectric point has slight dependence on the composition of mixture. The absorption ability of the studying polyampholyte gels with respect to surfactants was determined. It was shown that it depends on the ratio of positive and negative charges of the polyampholyte network.

THE SWELLING BEHAVIOR OF POLY(VINYLCAPROLACTAM) GELS IN AQUEOUS SOLUTIONS

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The swelling behavior of poly(vinylcaprolactam) (PVCa) gels was studied as a function of temperature in aqueous solutions. The specific feature of PVCa gel is the volume phase transition in water in response to temperature change. PVCa gel undergoes a volume - phase transition from swollen to collapsed state upon the increase of temperature. The temperature-induced phase transition of PVCa gel is reversible.

The effect of surfactants (cetylpyridinium chloride (CPC), sodium dodecylbenzenesulfonate (SDBS) and triton X-100) on swelling behavior of PVCa gel as a function of temperature at various surfactant concentrations was studied. It was shown that the swelling behavior of the thermosensitive PVCa gel in surfactant solution depends on the kind and concentration of the surfactant and on the temperature. The addition of the surfactant raises the transition temperature of the gel as compared to the surfactant-free system. In the presence of SDBS and CPC at concentrations above the critical micelle concentration the extra swelling of the gel was observed. The absorption of CPC and SDBS by the PVCa gel as the function of temperature was determined.

The other swelling experiments were performed with the PVCa gel in the presence of organic compounds. The swelling of the PVCa gel in the presence of the organic compounds (4-nitrophenol, 1-naphthol, pyrogallol) was studied. The effects of the additives on the swelling behavior were explained by considering the adsorption.

MICELLES IN SOLUTIONS OF CHARGED DIBLOCK COPOLYMER IN SELECTIVE SOLVENTS.

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A theory for water solutions of polyelectrolyte(A)/neutral(B) diblock copolymers is presented for the case when B-blocks are extremely hydrophobic. At very low concentrations copolymer chains form dense B-balls with swollen charged A-tails. At higher concentrations a formation of micelles takes place. Equilibrium properties of these micelles are investigated within scaling approach, a special attention being paid to distribution of the counterions. A complete diagram of relatively dilute solutions under consideration is constructed in the variables: block-copolymer concentration c — parameters of the copolymer chains (N_A , N_B , a (monomer size), h (fraction of charged links in A-block), γ (interfacial tension between B-links and water)).

At sufficiently low c all counterions are free and are not held near the chains. For rather high c a counterion condensation on the micelles takes place, so that most of the counterions are located within the crown of the micelle. This condensation may accompany the formation of micelles (at CMC), or at some values of the copolymer parameters it may take place at higher than CMC concentrations, hence there are regimes of "strongly charged micelles" and "weakly charged micelles". We calculated the free energy of a micelle made of certain number m of block copolymer chains and found the critical size for any set of the parameters characterizing the system.

The blob-picture of the micelle corona is determined by sizes of two blob types: by the so called "concentration blobs":

$$D_k = D_0 \exp(\alpha k)$$

where D_0 is the size of minimal blob, α is the parameter; and by the "electrostatic" ones:

$$D = u^{-3/7} h^{-6/7} a$$

where $u = e^2/\epsilon a T$. For strongly charged polyelectrolytes a tight packing of concentration blobs disappears and loose packing of electrostatic blobs occurs. For this case a structure of the corona has a appearance of stretch electrostatic blob chains.

PHASE TRANSITION BEHAVIOR OF POLYELECTROLYTE GELS WITH VARIABLE DEGREE OF IONIZATION

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Recently there appeared some experimental results on nonmonotonic conformational behavior of polyelectrolyte macromolecules and gels with the increase of the degree of ionization α during titration: after the initial swelling polyelectrolyte chains undergo sharp collapse transition at some critical value of α_{cr} .

In this paper we have shown that this unusual behavior can be explained by the partial formation of ion pairs, especially in the collapsed phase of low polarity. We have reconsidered the theory of polyelectrolyte gel collapse taking into account the possible formation of ion pairs with subsequent aggregation into ionomeric multiplet structure and the dependence of dielectric constant on the volume fraction of polymer inside the network. The new supercollapsed state of the gel which is close to the densely packed limit was found. In this state all the counter ions form ion pairs which are further organized into multiplets. This makes the supercollapsed state competitive with the swollen one. When α is initially increased the macromolecule (or gel) swells due to the increase of osmotic pressure of counter ions, but simultaneously supercollapsed ionomeric phase becomes relatively more favorable thermodynamically and at α_{cr} an abrupt collapse from the swollen to supercollapsed state takes place.

INTERACTION OF POLY(METHACRYLIC ACID) HYDROGELS WITH POLY(ETHYLENE GLYCOL)

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The interaction of poly(methacrylic acid) (PMAA) hydrogels with linear polymer poly(ethylene glycol) (PEG) was investigated. It was shown that PEG macromolecules penetrate in the swollen PMAA network and form there intermacromolecular complexes (IMCs) with PMAA through hydrogen bonds between oxygen atoms of PEG and carboxy groups of PMAA. These IMCs are also stabilized by hydrophobic interactions.

The composition and the effective dissociation constants of the IMCs were determined. It was shown that the increase of the chain length of the linear polymer results in a strong decrease of the effective dissociation constant of the IMC.

The distribution of PEG in the network volume was studied by IR-spectroscopy. It was found that in deficiency of PEG the complex forms essentially in the outer layer of the gel and at the excess of PEG the distribution of PEG in the gel volume becomes even. Thus, one can assume that the transport of polymer into the gel occurs through a repetitive interpolymer exchange reaction, that is, by layer-by-layer displacement of linear polymer from the periphery to the center of the gel specimen.

The complex formation influences significantly the conformational state of the swollen network. The swelling behavior of the IMC was studied as a function of pH, temperature, concentration and molecular weight of PEG. It was shown that at very low concentrations of PEG the network collapses due to the formation of hydrophobic IMC. At concentrations of PEG in solution ca.10 wt.reentrant network swelling takes place. The reswelling is accompanied by jumpwise penetration of PEG in the gel. The reentrant swelling transition in such system was recently predicted theoretically. In the present work this effect was established experimentally.

The PMAA gel - PEG complexes are very sensitive to pH changes. A phase transition of the complex PMAA gel - PEG from swollen to the collapsed state determined by the concentration of low molecular weight acid in the solution was observed. In the solution of strong acid the dissociation of PMAA is suppressed. This leads to the lowering of the osmotic pressure of protons in the network which is favorable for collapse.

The properties of PMAA gel - PEG complexes can find practical applications in novel controlled release drug delivery systems or for creation of polymer membranes with regulated permeability.

POLY(METHACRYLIC ACID) HYDROGELS - NONIONIC SURFACTANT COMPLEXES

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Poly(ethylene glycol) (PEG) - based nonionic surfactants form stable complexes with linear poly(methacrylic acid) (PMAA), but such complexes in PMAA hydrogels are poorly understood. In this work we study the complex formation between PMAA hydrogel and nonionic surfactant PEG tert-octylphenyl ether (Triton X-100).

The composition of complexes and the constants of distribution of Triton X-100 between the gel phase and solution were determined with UV-spectroscopy. It was shown that nonionic detergent is effectively concentrated in the network.

The absorption of the surfactant induces the conformational changes in PMAA hydrogel. The conformational behavior of the gel depends strongly on pH and on the initial concentration of the surfactant. A sharp network collapse is observed at very low surfactant concentration. Further increase of the surfactant concentration results in a gel reswelling. These conformational changes of the gel are analogous to conformational changes of linear PMAA in Triton X-100 solutions. The magnitude of the conformational changes increases with lowering pH.

At low surfactant concentrations the PMAA gel - Triton X-100 interactions can be due to hydrogen bonding between PMAA carboxy groups and PEG oxygen atoms. The saturation of hydrogen bonds results in the formation of hydrophobic complex, which is responsible for the gel collapse. The aggregation of hydrophobic residues of the surfactant stabilize the complex. When all hydrogen bonds are saturated, another mechanism of PMAA - Triton interactions is coming into play. Nonionic surfactant accumulates around the hydrophobic complex and exerts uncoiling of the aggregated complex, which results in a gel swelling.

The interaction of PMAA gel with Triton was compared with one with PEG of the same degree of polymerization as PEG chains of Triton molecules.

PEG is known to form complexes with PMAA hydrogels via hydrogen bonding. The hydrophobic interactions are of great importance for stabilization of these polycomplexes. The introduction of hydrophobic substituent in PEG macromolecules permits to reveal the role of hydrophobic forces.

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INTERACTION OF SLIGHTLY CROSS-LINKED POLY(DIALLDIMETHYLAMMONIUM
CHLORIDE) GELS WITH INORGANIC SALTS AND SURFACTANTS. PHASE
TRANSITIONS AND STRUCTURE OF COMPLEXES

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The interaction of slightly crosslinked positively charged gel of poly(diallyldimethylammonium chloride) (PDADMACl) with sodium salts of halogens and alkylsulfates with different hydrophobic chain length in aqueous media has been studied. At the critical concentration of sodium iodide a phase transition of the network in collapsed state is observed. The presence of other inorganic salts does not initiate the collapse of the network. The decrease of the charge density of the cationic network by copolymerization of cationic monomer with acrylamide results in disappearing of the phase transition. In this case usual polyelectrolyte contraction of the gels in the presence of the low molecular salts is observed.

These results are explained by the formation of ion pairs and multiplets (ionomer effect) for the charged enough networks in the collapsed state. As a result, collapsed ionomeric state of the network becomes competitive with swollen polyelectrolyte state at high enough fraction of ion-containing links and large dipole moments associated with ion pairs.

Interaction of the cationic network with anionic surfactants results in jump-wise collapse or significant shrinking of the gels due to formation of polymer-surfactant complexes. SAXS study demonstrate high ordered BCC type structure for the complexes formed by sodium dodecyl and tetradecyl sulfates.

The relation between size and quantity of microgel and the conditions of interpolymers synthesis

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The purpose of the work is an investigation of the processes of the formation of macromolecular compounds of the new type (interpolymers), by means appraisal of microgel size and quantity presenting in the polymers formed by irreversible chemical reaction in solution between two incompatible polymers containing mutually reactive functional groups in the repeating units of macromolecules (by Friedel-Crafts reaction between poly-1,1,2-trichlorobutadiene-1,3 and polystyrene).

The calculation was made from dates of the angular light scattering by the Lange-Gunie method.

Wellknown the reactions of interpolymer complexes formation proceeding by reversible interactions between the functional groups arranged the along polymer chains.

Unlike this the information about irreversible interpolymer reactions proceeding by interaction between the functional groups of incompatible polymers is very poor.

Under definite conditions these reactions give soluble lengthwise polymers with covalent bonds between different chains (interpolymers), which combine the properties of initial homopolymers or assume in the reaction course new valuable properties and can easily be processed from solution.

In the course of interpolymer reaction an alternation of inter- and intramolecular interactions of functional groups of initial and interpolymer macromolecules participating in the reaction take place.

It was found that the polydispersity and MM of initial polymers influence on the correlation between inter- and intramolecular processes.

So, the reaction between fractions of the initial polymers leads to intermolecular interaction.

It was remarked that at $M_{WPTHB} \ll M_{WPS}$ prevails intramolecular interaction.

The reactions offer new possibilities in the sphere of chemical modification of polymers.

MICROHETEROGENEITIES IN COLLAPSED POLYELECTROLYTE GELS

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Recently it was theoretically predicted that weakly charged polyelectrolyte networks in a poor solvent should undergo a microphase-separation transition. There are three possible reasons for microsegregation: polyelectrolyte effect (the competition between the attraction of uncharged parts of the gel and electrostatic repulsion coupled with osmotic pressure of counter ions in charged domains), ionomer effect (the formation of ion pairs multiplets) and vitrification effect (the formation of glassy kinetically frozen structures due to phase separation intercepted by vitrification).

The aim of the present work is to study possible microheterogeneities in polyacrylamide gels, containing up to 10% of cationic (diallyldimethylammonium bromide) or anionic (sodium and cesium methacrylate) units, in poor solvent. The quality of solvent was varied by changing the fraction of poor solvent - ethanol in water-ethanol mixture.

Non-equilibrium structures due to vitrification effect were found for both both cationic and anionic gels in water-ethanol mixtures containing more than 70% of ethanol, when the gel samples swollen in water were immersed in poor solvent. It was shown that the charged gels are vitrified in a highly swollen state in comparison with the uncharged gels. The greater the charge density of the gel, the larger the relative mass of the gel in the vitrified state. The relative mass of the gels in kinetically frozen state decreases with decreasing the crosslinking density.

To characterize the microscopic structure of the gel the SAXS technique was employed. It was shown that for weakly charged gels the formation of kinetically frozen structures results in the increase of the value of scattering exponent from 1.7 to 3.5 which indicates to the appearance of microstructure with smooth phase boundaries. For cationic gels with 10% of charged units we observed the sharp increase of the scattering exponent at lower ethanol concentrations which occurs simultaneously with the gel collapse. This result was explained by the formation of microstructure due to ionomer effect. The ionomer effect manifests itself only at sufficiently high concentration of charged groups when ion pairs easily form multiplets. No SAXS scattering maxima was detected which is apparently due to high irregularity of the obtained microstructures.

INTERPOLYMER COMPLEXES AND COMPOSITES OBTAINED BY MATRIX POLYCONDENSATION OF SILICA ACID

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Matrix polycondensation of silica acid forming by tetraacetoxysilane (TAS) hydrolysis in benzene in the presence of polyethylene glycol (PEG), polyvinyl caprolactam, or polyvinyl acetate has been studied as well as composition and properties of the resulting complexes and composites depending on component concentrations, molecular weight of a polymer, temperature, and TAS hydrolysis degree. Complexes are stabilized by hydrogen bonds.

In dilute solutions, non-soluble complex matrix – poly(silica acid) (PSA) is shown to be the only product of the process. In semi-dilute solutions, the final products may represent transparent solution or gel. Under these conditions, the product is enriched in a matrix which can provide it's solubility; free PEG segments belonging to the particles of the product are capable to crystallize.

On usage of PEG as a matrix, the composition of the complex formed in dilute solutions is constant (PSA:PEG=1:2 in unit moles) at low TAS concentrations; this may reflect the formation of linear PSA under the control of macromolecular matrix since each unit of linear PSA is capable to bind two units of PEG. If molar ratio $\text{Si}:(-\text{O}-\text{CH}_2-\text{CH}_2-)>1:2$, the product comprises the complex and the excess of PSA.

The products obtained both in dilute and semi-dilute solutions of PEG are not separable onto free components by multiple extraction unlike the model product obtained by mixing of previously prepared suspension of PSA with PEG in benzene (adsorption of PEG on PSA is reversible in this case).

Two fractions of PEG are found in the obtained matrix composites; one fraction is attributed to the polymer segments which are inside the complex particles (comprising presumably linear PSA), while another, to the segments which are on the surface of the particles. In the model complex, the first fraction is absent.

Acknowledgment. The research described in this publication was made possible in part by Grant 93-03-18096 from the Russian Foundation for Fundamental Investigations and Grant N2S000 from the International Science Foundation.

Behavior of Nematic Polymer Solutions near the Nematic - Smectic A Transition.

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Some elastic constants of nematic liquid crystals show a drastic pretransitional increase in the vicinity of the nematic - smectic-A transition due to smectic-like fluctuations. The presence of such fluctuations causes a strong pretransitional increase in the bend elastic constant $K_3 = K_3^0 + \delta K_3$ where K_3^0 is a background term in the absence of smectic-like fluctuations and K_3 is a temperature sensitive term.

This contribution presents the study of pretransitional behavior of dilute (< 5 wt.%) solutions of side-mesogenic-group polyacrylates ($8530 < M_w < 46300$) in a low molecular weight liquid crystal, octylocyanobiphenyl (8CB). Temperature dependences for polymer solutions were fitted to the theory of P.G de Gennes* based on the analogy between superconductors and smectics A: $\delta K_3 \propto (T - T_{NA})^{-\beta}$ with an exponent $\beta = 0.67$.

It has been shown that

- i) adding of polymer molecules causes the bend elastic constant to increase;
- ii) the increase in K_3 is controlled by the number of dissolved polymer chains C/N (the smaller N the higher K_3 for the same concentration C);
- iii) the effect is mainly due to the background term K_3^0 whereas the value of the exponent is $\beta \approx 0.65$ within the experimental error for both pure solvent and polymer solutions.

*P. G. de Gennes, Solid State Commun., 10 (1972) 753.

SELF-ASSEMBLING IN THIN FILMS OF MESOPHASE LINEAR AND CYCLOLINEAR POLYSILOXANES

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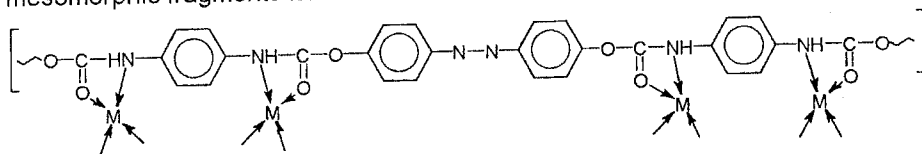
Some novel linear and cyclolinear (CLPOS) polyorganosiloxanes without classical mesogenes in their macromolecules can form thermotropic mesophases which can be classified as columnar mesophases. In the study the π/A -isotherms for a series of CLPOS were investigated to clarify their phase and mesophase behaviour. Similar to polydimethylsiloxane (PDMS), which is known to be able to spread and form thermodynamically stable monolayers, all CLPOS studied were capable of spreading and building LB films in vicinity of 20 $\text{\AA}^2/\text{repeat} [\text{Si}(\text{R}_2)\text{O}]$ unit, which seems to correspond to LB-film formation, where oxygens are fixed on the water surface and the side groups are directed to the air. Unlike PDMS, CLPOS self-assemble stable multilayers the thickness of depends on the surface pressure π . The transition from the monolayer to bi-, tri-, (up to seven) layers is partly reversible and characterised by sharp steps in π/A -isotherms. The steps in are closely related to the molecular structure. A model is suggested, in which the steps are treated as a result of a sliding mechanism and crystalline and mesophase behaviour.

The financial support of SFB-239, University of Ulm is highly acknowledged.

SYNTHESIS AND INVESTIGATION OF THE LIQUID CRYSTAL POLYURETHANE METAL COMPLEXES

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Polyurethane metal complexes have been synthesized on the basis of the polyoxyethylenglycol, Cu(II) and Fe(III) chlorides, symmetrical aromatic diisocyanates and azoaromatic compounds; the complexes have been properties of the thermotropic liquid crystals. The temperature of the mesophase transition lies in range 20–110°C and depends from the 3d-metal nature and from the structure of the aromatic diisocyanates. Specific electric resistance synthesized nematic liquid crystal systems is 10^3 – 10^5 Ohm·cm. Was established considerable decreasing of the specific electrical resistance in the region of the mesophase transition. It was cleared character of coordination interaction of the 3d-element ions on the polyurethane chains. The presence of both coordinations from the ether and urethane was showed by IR-spectroscopy method. The supposed structure of the mesomorphic fragments is:



M = Cu, Fe

The work is supported by the Russian Found of Fundamental Research.

PECULIARITIES OF LIQUID CRYSTALLINE ORDERING IN MELTS OF POLYMER WITH DIFFERENT CHEMICAL STRUCTURE.

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Liquid crystalline (LC) order formation in flexible main chain polymer melts in majority of studied cases is accompanied by "polymer effect". This effect manifest itself in (a) greater values of order parameter at T_{is} (temperature of transition of isotropic melt to LC state) than corresponding values for low molecular weight LC; (b) dependence of both T_{is} and thermodynamic characteristics of transition on mol.weight and (c) broadening of biphasic region. One can suppose that the scale of this effect is determined to a large degree by spacer properties. Using the approach developed by the authors (based on joint employment of X-ray structural analysis, DSC and calculations of spacer conformations in the frame of rotational isomer model together with direct determination by IR spectroscopy of orientational and conformational characteristics of macromolecular fragments) local conformations of molecular fragments and conformations of chain as a whole were analyzed.

It was determined that the degree of LC ordering depends on flexible spacer properties, in particular on energy difference between gauche and trans-isomers. For example, in the case of trans-isomer preference (corresponding to methylene sequence as a spacer) substantial extension is observed both for monomer fragment and chain as a whole; gauche-isomers preference (ethylene glycol sequence as a spacer) leads to disordered conformation of spacer; in some specific cases hairpin configuration of spacer is observed. Spacer configuration influences ratio of attractive and repulsive forces during LC ordering and determines "the scale of polymer effect".

New data on conformational ordering of polymer chain as a whole in the temperature interval of LC state existence, on effect of LC state formation on mesogen conformations and on peculiarities of LC order formation in melts of copolymers with various spacer lengths are obtained.

Several factors important for broadening of biphasic region during LC - isotropic melt transition are discussed, together with correlation between width biphasic region and polymer chemical composition. Derived results are matched with existent theories of LC ordering in polymer melts.

MATHEMATICAL MODELS OF SELF-ASSEMBLY.

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The idea of self-assembly arose due to the experimental discovery of appearance of VTM particles in mixtures of theirs components. The approach was applied to explanation of formation of biologically important nano and supermolecular structures.

The main peculiarity of the self-assembly is formation of structures consisting of big numbers of invariable elements. The structure formation can represent either a successive addition of elements or hierarchic combination of structures to more large ones. Bonds between these elements can be directed or undirected and possess different life times and energies. Kinetic parameters of self-assembling can change during the structure formation.

These features are taken into account in some mathematical models of self-assembly based on general approach proposed by A.M.Leontovich. These models describe kinetics of interaction and formation of structures by use of oriented graphs with marked vertexes and edges. In this case a topology was taken into account but no space disposition and organization of elements.

Systems of nonlinear differential equations describing the self-assembly kinetics can be formulated both for elements and bond blocks concentrations. In the latter only the structure fragments are characterized independently of their positions inside the structure. Such consideration allows to determine concentrations of fragment similar to genes in chromosomes, promoters, exzons and motives in DNA.

The study of developed mathematical models by analytical and numerical methods had led to clearing of general features of linear fragments under binary and non-lokal interactions. The particular processes of poly- and copolycondensation were distinguished that are described by statistical methods. Some peculiarities resulting from "neighbor effects" inside the first sphere were studied.

STUDY OF ORDERED STRUCTURES OF L- α -POLYGLUTAMIC ACID COVALENTLY BONDED WITH DIFFERENT DYES IN LB-FILMS.

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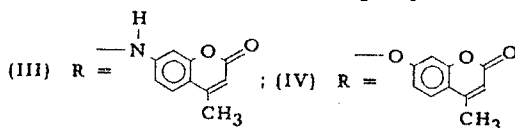
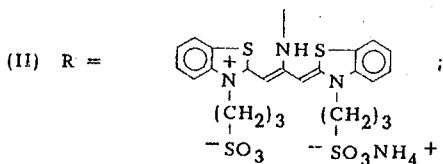
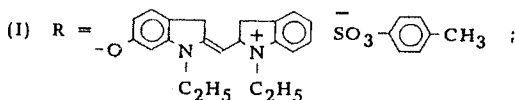
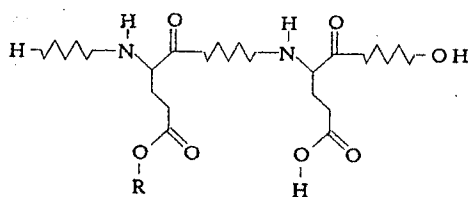
++ Physics Institute Academy of Science, 130023 Changchung, P.R. China

L- α -Polyglutamic acid covalently bonded with oxy-, aminocarbocyanine, 7-oxy-, 7-aminocoumarines are obtained by peptide's chemistry methods - DCC or NCA. Each of covalent bond was proved by ^1H , ^{13}C NMR, IR and UV - spectras. An average number of dye molecule per on polyaminoacid molecule (MM~ 6000) was calculated by NMR - method and from the absorption spectras measured in LB-films and in delute solutions for carbocyanines derivatives.

The properties of photochromic polyaminoacids were studied in monomolecular layers at the air/water interface. For carbocyanine's derivatives the comparison of the UV/vis spectra of LB-film and the polymer solution reveals a strong aggregation of chromophores in the LB-film. By polarised UV/vis spectroscopy a in plane orientation of the chromophores was found which is typical for "hairy - rod" like polymers. The influence of irradiation's time is shown on some reorientation or decomposition of H-aggregates in LB-films.

Polyglutaminoxycarbocyanine LB-film have been investigated by the out of plane optical dichroism method too. The absorption spectras are explained in term of formation of different molecular aggregates such as dimers and H-aggregates (side-by-side interaction). The ordered parameter of molecular chromophores characterised by a value of coefficient P_2 at the second term in the expansion of a molecular distribution function over Legendre polynomias was found for these different aggregates.

"The sandwich structure" from variable monolayers (polyglutamincoumarines (III, IV) and polyglutamincarbocyanines (I, II)) are fabricated for optical tests. UV/vis spectra demonstrated new absorption maximum shift. The exist of exiting effect is discussed in this work as well.



POLYMER ULTRATHIN FILMS WITH IMMOBILIZED PHOTOSYNTHETIC REACTION CENTER PROTEINS

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Lipid monolayers with immobilized photosynthetic reaction center proteins (RCs), isolated from *Rhodobacter sphaeroides* (wild type) were investigated to evaluate lipid-protein interaction. RCs are protein-chromophore complexes which consist of three protein subunits (L, M, H) and provide vectorial photoinduced electron transfer across the cell membrane. Monolayers were prepared with synthetic lipid-like monomers: N-acryloylphosphatidylethanolamine (ACPE), tetracos-11,13-diyne acid (DYA) and various natural lipids.

The monolayer characteristics were analyzed to determine the optimum conditions for stable film as a function of salt concentration, pH and temperature in water subphase. ACPE has of the polymerizable groups in hydrophilic part and DYA - in hydrophobic part. The maximum polymerization rate for monomers was $2,5 \cdot 10^{-4} \text{ s}^{-1}$ for ACPE monolayers and was $6,5 \cdot 10^{-2} \text{ s}^{-1}$ for DYA monolayers. The rate of polymerization for mixed ACPE-RC and DYA-RC monolayers was decreased about ten times depending on the monomer-RC ratios in comparison with corresponding values for pure lipid-like monomers on air/water interface.

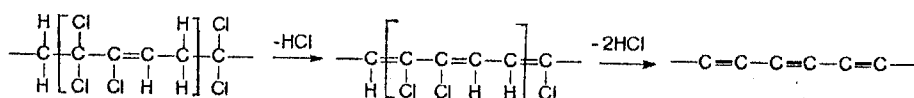
To evaluate structural integrity of lipid-RC monolayers, the spectral properties of their multilayer films onto solid supports were investigated. The optical and photoelectrical measurements in the electrode/thin organic film/electrode systems provide evidence for a degree of orientation of these proteins at interfaces. The preferential orientation of the RCs on supports was found to be dependent on lipid nature. The sign of the photopotential (plus on the SnO₂ support for ACPE - *Rb. sphaeroides* RCs) provides evidence that the H-subunits in such monolayers faces preferentially the air-buffer interface so as to interact with water. The same orientation observed in the monolayers of individual RC. In contrast, was seen with DYA - *Rb. sphaeroides* RCs films, has the minus sign on the electrodes, indicating that the H-subunits preferentially oriented towards the air. Obtained results show an applicability of the films as material for biosensors and optoelectronic devices.

CARBONIZATION OF THE SURFACE BY CHEMICAL DEHYDROCHLORINATION OF POLY-1,1,2-TRICHLOROBUTADIENE.

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A mixture of the alcoholic solution of KOH (40 vol.-%) and tetrahydrofuran (60 vol.-%) brings about exhaustive dehydrochlorination of poly-1,1,2-trichlorobutadiene-1,3 (PTCB) with carbene formation:



A strong absorption band of the triple bond appears 2170cm^{-1} in the IR spektrum of the reaction product. We investigated electronic structure of the polymer by means of Auger electron spectroscopy for determination of the nature of chemical bonds in dehydrochlorinated PTCB.

The 100-150 mk thick PTCB films can be dehydrochlorinated by this method only on the surface, a thin carbonized polymer layer being chemically bonded with the main polymer mass.

A study of the surface of dehydrochlorinated film by means of X-ray photoelectron spectroscopy showed that the reaction products contain also chlorine (0,5%), oxygen (6,5%) and nitrogen (~1%) in addition to carbon (~93%).

The PTCB films reveal high adhesion to metals and other materials (PTCB is used as an adhesive for fastening the rubber with metal). The treatment of PTCB films by the dehydrochlorinated mixture is a simple and accessible method for carbonization of metal, rubber and another surfaces.

The carbonization increases essentially the mechanical strength of polymer films and retains elastic properties.

SELF-ORGANIZATION OF NANOMETER SURFACE LAYERS DURING FRICTION OF ALIPHATIC POLYMERS

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During friction self-organization there are nanometer outer layers forming on the surface of aliphatic polymer. They sharply differ from the subsurface layers and the material in the depth.

The nanometer thin outer layers and the subsurface layers of polyethylene (PE), ultra-high molecular weight polyethylene (UHMWPE), and some polyamides have been investigated by X-rayphotoelectron spectroscopy, mass-spectroscopy, IR-spectroscopy.

It has been shown that the reason of this unusual structure of nanometer layers is connected with high mobility of aliphatic polymers and, specially, with the presence of low molecular destruction products.

In some known cases of friction, specific for each polymer becomes be able to orient itself in the surface layers the polymer molecule or its part not only in the direction of friction, but also in the depth of sample during self-organization of the surface.

As the result, the particals having low surface energy seek to occupy the thin nanometer outer layer of the surface.

So, after friction in air the chemical structure of nanometer layers of UHMWPE is characterized not by oxidation of the surface outer layer but by decreased content of the polar oxidized groups.

The surface nanolayers of polyamides is enriched in some cases of friction in the olephinic fragments having low surface energy.

Consideration of the phenomenon of nanolayers as a result of "two-measure" process of self-organization offers a possibility to explain some phenomena unclear today, and first of all apparent active course of tribochemical processes not in the surface, but in the subsurface layers of polymer. The reasons of the dependence of the times and the friction temperature on the change of chemical structure of the surface outer layer become clearer.

Acknowledgement. The authors are grateful to the prof. A.Perzin for the support of this work.

SURFACE DYNAMICS OF PHOTOOXIDIZED EPDM RUBBER

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It is well established now that polymer surfaces are capable to reconstruction. Such reconstruction may occur when the composition of polymer surface layer is changed in comparison with the bulk one as a result of modification by grafting, plasma treatment, etc. The same effect can take place upon variation of the polarity of the medium contacting with polymer. In both cases, the driving force for such reconstruction is minimization of the free surface (interfacial) energy. The kinetics of this process depends on its mechanism, which may be different for distinct systems and determined both by macromolecular (segmental) diffusion and reorientation of individual groups. However, there are not quantitative investigations of the surface reconstruction kinetics up to now.

We have studied the surface dynamics of thin films of the EPDM rubber after their photooxidation in air and, by using IR spectroscopy and wettability methods, obtained the following main results.

1. At early stages of photooxidation, when the concentration of oxygen-containing groups formed is relatively low, this groups are buried into the bulk from the polymer surface and surface energy does not increase. And what is more, certain decrease of the surface energy takes place due to "loosening" of the polymer surface layer during its rearrangement.

2. When air is replaced by water, the "reverse" reconstruction of the surface layer of photooxidized rubber occurs. It means, that oxygen-containing groups gradually emerge at the interface. The rate of this process and the degree of the free interfacial energy lowering depend on irradiation dose (content of polar groups in the rubber film).

3. As followed from the analysis of the experimental data obtained by "prolonged wetting" method, such reverse reconstruction accompanying by the polar groups accumulation at the photooxidized rubber/water interface can not be described within the framework of the simple model of polar groups reorientation (turnover) but it is a diffusion-controlled process.

This conclusion is in an agreement with the results obtained for the prevulcanized EPDM films. For such films, even at low degrees of photooxidation, no surface rearrangement was detected; the polar groups formed were remained at the polymer/air interface, obviously owing to the loss of macromolecule translational mobility in surface layer.

ASSEMBLY OF MULTICOMPONENT PROTEIN SUPERLATTICES BY MEANS OF ELECTROSTATIC LAYER-BY-LAYER ADSORPTION

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Multilayer films which contain ordered layers of more than one protein species were assembled by means of alternate electrostatic adsorption mostly with positively charged poly(ethyleneimine) (PEI), poly(dimethyldiallylammonium chloride) (PDDA) or with negatively charged poly(styrenesulfonate) (PSS)[1,2]. Water soluble proteins used are cytochrome c (Cyt), myoglobin (Mb), lysozyme (Lys), histone f3, hemoglobin (Hb), glucoamylase (GA), glucose oxidase (GOD) and catalase (Cat). Charged protein layers formed molecular superlattices with linear polymers acting as glue or filler. The assembly was monitored by a quartz crystal microbalance - QCM, UV spectral measurements and by scanning electron microscopy. Linear film growth was observed up to at least 25 molecular layers.

Four different types of superlattices were elaborated: 1) The assembly of Mb and Lys, both positively-charged, was realized in alternation with PSS in the form of $\{PEI/PSS + (Mb/PSS)_2 + (Mb/PSS/Lys/PSS)_4\}$. As well, a superlattice containing GOD and GA, both negatively charged at pH 6.8, was assembled in alternation with polycation PDDA in the following architecture: $\{(PEI/PSS)_2 + (PDDA/GOD)_2 + (PDDA/GOD/PDDA/GA)_5\}$. The frequency shift for the four-layer unit was $-\Delta F = 800 \pm 50$ Hz ($-\Delta F$ is proportional to film mass increase). This value is consistent with frequency shifts for separate two - components adsorption measured for GOD/PDDA and GA/PDDA films. 2) The assembly of oppositely-charged (at pH 6.5) Lys and GOD consists from Lys and GOD layers separated by a polycation/polyanion bilayer: $\{PEI/PSS/PEI + (PSS/Lys)_2 + PSS/PEI + (GOD/PEI)_6\}$. 3) Hb was assembled as "positive" unit at pH 4.5 (in alternation with PSS) and as "negative" unit at pH 9.2 (in alternation with PEI). 4) Superlattice consisting from alternating Montmorillonite clay, PEI and GOD monolayers was also assembled.

These biomolecular architecture open a way to construct artificially orchestrated protein systems that can carry out complex enzymic reactions.

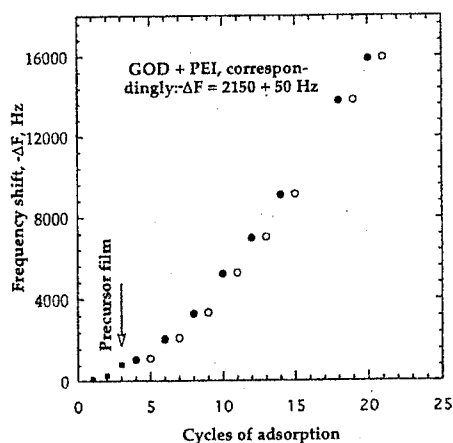


Fig.1 QCM frequency shift ($-\Delta F$) due to cycles of alternate GOD/PEI adsorption. () GOD adsorption steps, and () PEI adsorption steps. Steps 16-18 were continued without intermediate drying, but linear mass increase still apparent.

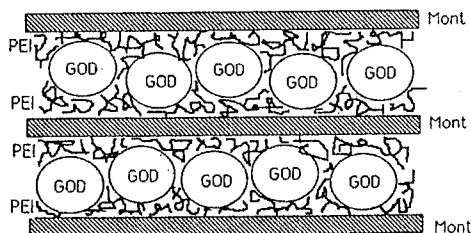


Fig.2 Schematic simplified illustrations of protein superlattice: GOD/ PEI/ Montmorillonite/ PEI multilayer.

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FORMATION OF TWO-DIMENSIONAL ORGANIC NETWORKS ON LIQUID SURFACES AND SOLID SUBSTRATES

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The properties of monolayers of novolac and diglycidyl ether of bisphenol A type epoxy oligomers on the surface of water and aqueous solution of amine based curing agent were studied. Using surface balance technique and FT-IR spectroscopy, it was found that the time evolution of surface pressure and surface area of the monolayers on pure water is controlled by the chemical reactions of these oligomers with water and carbon dioxide. In bulk the similar reactions may proceed only under severe conditions. The specific reactivity of epoxy oligomers in a onelayer organized system at the air-water interface is enabled by the increased concentration and the mobility of protons in a thin layer of water adjacent to the monolayer, and by the basicity of the epoxy groups of the oligomers. The conditions under which the reactions of epoxy groups with water are suppressed and polycondensation of epoxy and amine groups prevail were determined. As a result of the polyreaction, the collapse pressure of the monolayer increases 15 times and the limiting area increases 2.5 times. Surface reactions of epoxy oligomers are shown to be topochemical in nature; the kinetics of these reactions may be described by the Avrami-Erofeev equation. The magnitudes of the parameters of this equation, which were determined for the monolayers of each of the oligomers, lead to the conclusion that, generally, the dynamics of epoxy oligomer monolayers is controlled by chemical transformations in and rearrangement of the surface layer. The composition of a two-dimensional network of epoxy polymer was evaluated. The fabrication of the Langmuir-Blgett films of this polymer on the surfaces of various solid substrates is reported.

MODEL CALCULATIONS FOR
THE GROWTH OF SURFACE LAYERS DURING
SPINODAL DECOMPOSITION IN POLYMER MIXTURES

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By numerical integrating of the Cahn-Hilliard equation in two-dimensions, we have studied the growth of surface layers during spinodal decomposition in a binary polymer mixture (of a critical concentration), disposed as a thin film between similar impenetrable walls. The short-range surface interactions under consideration ensure the adsorption of an A-component of the unstable polymer mixture and, depending upon their force, an A-rich phase nonwets or wets a single wall in thermal equilibrium.

As substrate forces are weak, the surface layers have a structure similar to a phase-separated one within the film bulk. Their thicknesses, h , are found i) to grow at long time according to a power-law $h(\tau) \propto \tau^\alpha$ where $\alpha \approx 1/3$ (the asymptotic behavior is in agreement with the theory of the domain growth developed by Lifshitz-Slyozov) and ii) to be about the coarsening domain sizes inside the film bulk.

In the case of strong substrate forces the initial, fast, slow and final stages of the adsorption process may be distinguished. The fast growth of thin plated adsorption layers, formed during the initial stage of spinodal decomposition, is established to be described by an exponent value $\alpha \approx 1/3$, which results from diffusion of individual macromolecules of the A-component into the layers. Throughout the next stage the surface layers thicken much more slowly ($\alpha \approx 0$). In the conditions of strong surface interactions the phase separation results in strong concentration modulations inside the polymer films and the emerging depletion zones are supposed to provide the pinning effect. During the final stage of the process the A-rich phase domains, initially nucleated in the film bulk, drift towards the walls and coalesce with the adsorption layers; now it is the growth of the surface droplets (as well as in the case of weak substrates) which is responsible for the time changes of the surface layers. For strong substrates the surface layer thicknesses are observed to be significantly less than the growing domain sizes within the thick film bulk.

This work was supported by the Russian Basic Research Foundation (Grant No. 93-03-05466) and the International Science Foundation (Grant No. M5K000).

DYNAMIC AND THERMODYNAMIC NON-LINEAR EXCITATIONS
IN POLYACETILENE, POLEENE, AB-POLYMERS

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Abstract

Regularity of the structure of the above quasi-one-dimensional systems and the following peculiarities of the electron-phonon interactions in them are taken into account: nearest and second neighbor for linear polymers.

At some self-consistent approach the spin, charge, creation energy, width, band energy, position of localized level of polaron states in linear polymers has been investigated [1]. These states may play important role for processes of charge transfer on polyacetylene, polycarbonitrile, poly-1.6-heptydyne and also some organic mixtures. With help [2] all dynamic and thermodynamic properties of these polymers has been calculated.

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SPATIAL STRUCTURES INDUCED BY STRETCHING OF ENTANGLED NETWORKS

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The modern small-angle neutron scattering experiments with swollen polymer networks lead to the discovery of a number of unexpected phenomena, the most spectacular one being the observation of "abnormal butterfly" effect. In this connection the density-density correlation function I_q , which determines the angular dependence of the scattering intensity at different spatial scales R (or wave vector $q \sim R^{-1}$), is calculated for strongly deformed, lightly cross-linked polymer networks. We use the replica variant of the tube model to take into account the entanglement effects.

In contrast to usual polymer liquids, where there are only thermally driven (annealed) density fluctuations, in polymer networks there are also frozen-in (quenched) fluctuations at large spatial scales R (significantly greater than the mesh size of the quasi-network). The source of quenched fluctuations is the random internal stresses because of irregularities in the chemical structure of the networks. It is shown that the correlation function I_q can be written as a sum of two terms $I_q = S_q + G_q$. Only the annealed fluctuations contribute to the first term S_q and this term is responsible for the normal butterfly effect. The second term G_q gives the contribution of the quenched fluctuations. For the parameters of the system which correspond to the experimental conditions, it is this term that produces the major contribution to the correlation function I_q and is responsible for the abnormal butterfly effect.

We also calculate the free energy functional for such "soft" solids taking into account liquid- as well as solid-like degrees of freedom at different spatial scales. Dynamics of the abnormal butterfly effect is examined using this functional. Relaxation of the internal stresses in such substances (as in solids) initially occurs at large scales: the abnormal butterfly pattern appears first on small wave vectors q and afterward is expanded to the range of larger q values. This evolution is in good agreement with that observed experimentally.

MICRODOMAIN STRUCTURES IN POLYMER SOLUTIONS (BLENDS)
NEAR GLASS TRANSITION TEMPERATURE

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Polymer solutions (blends) near glass transition temperature are relatively new objects of investigations as regards microphase separation transition.

Some years ago density microheterogeneties have been observed experimentally in polymer blends near glass transition temperature. To explain this phenomenon we suggest the model which is based on the assumption that near glass transition temperature the effects of nonlocal entropy should come into play. The magnitude of these effects and the radius of entropy nonlocality essentially depend on the temperature achieving the maximum value at the point near glass transition temperature. These entropy effects influence against the tendency to segregation. The effect of these entropy factors lead to i) the improvement of a compatibility of polymer solutions (blends), ii) microphase separation transition.

The phenomenon of microphase separation transition is studied in the weak segregation limit. The conditions of formation of different microdomain structures are analyzed. Stability of microdomain structures with respect to macrophase separation is also investigated. As a result, phase diagrams containing the regions of different microdomain structures have been obtained for polymer solutions (blends) near glass transition temperature.

**SPINODAL DECOMPOSITION IN POLYMER GLOBULE
WITH SECONDARY STRUCTURE**

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We consider the model "beads on the string" with the attractive two-particle and repulsive three-particle interaction. Besides external degrees of freedom (spatial coordinates) to each bead attributed the internal Ising variables modeled the polymer secondary structure. The "secondary structure" influence on the polymer chain behavior described by the additional term in Hamiltonian which has the Ising model form. The mean-square distance between adjacent beads $(i), (i+1)$ depends from the internal variables of these beads.

The order parameter of this system is distribution function of the chain end states, which connected with the beads density in standard manner [1]. In the volume approximation the free energy expansion near the spatially-homogeneous state over the order parameter was obtained. It was shown that at the definite conditions homogeneous state becomes unstable: the system undergoes spinodal decomposition into two macrophases. In the range of non-stability of phase diagram can exists a three types of segregated structures, differs by them quantities. A phase transitions between these structures were obtained.

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GLOBAL STATE OF THE POLYMER CHAIN WITH RIGID SIDE CHAINS WITH THE QUENCHED DISORDER.

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We consider here the model of heteropolymer with the mesogenic side chains with random anisotropic interactions between them. We have a system of hard rods with length b , linked by gaussian tails with mean-square distance a . These rods interacted by anisotropic potential:

$$\Phi(r_i, r_k, u_i, u_k) = W_{ik} \delta(r_i - r_k) P_2(u_i, u_k)$$

where r_i and u_i are the the center mass coordinate and tangent vector of i -th rod, respectively; $P_2(x)$ is the second Legendre polynomial; $\{W_{ij}\}$ are the statistically independent random variables with bimodal distribution:

$$G(W_{ij}) = (1-c)\delta(W_{ij} - W_0) + c\delta(W_{ij} - W)$$

Isotropic interaction term has given by the usual form:

$$H\{r_i\} = B/2 \sum_{ij} \delta(r_i - r_j) + C/6 \sum_{ijk} \delta(r_i - r_j) \delta(r_k - r_j)$$

Here B, C are the second and third virial coefficients, respectively.

In order to average over quenched disorder $\{W_{ij}\}$ we use the replica trick. In the framework of this method it was shown that in the temperature range corresponded to isotropic liquid globule:

(I) The freezing transition of the chain backbone configuration take place recently predicted by Shakhnovich et al.[1,2] for the polymer with random isotropic interaction. The polymer chain backbone configuration become thermodynamically authentic.

(ii) Below the "backbone freezing" temperature the side chains can exist in two states characterized by different degrees of thermodynamic authenticity. The system undergoes a first-order transition from the more fluctuated to the less fluctuated configuration of the side chains.

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Cubic Phases in Block Copolymers: "Proto Structure", Structure, and Density Projection

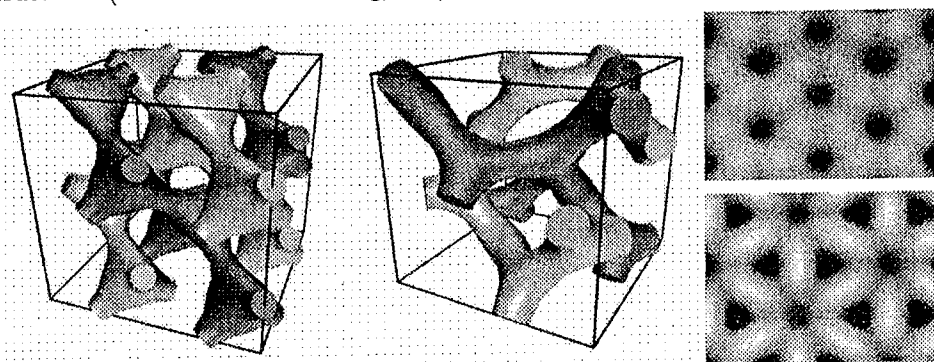
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The structure of a microphase-separated block copolymer in the weak segregation regime can be modeled by a superposition of a small set of density waves ("proto structure"). In the case of the highly symmetric cubic phases, the first order Fourier components with equal wavelength, equal absolute amplitude, and appropriate phases may or may not be sufficient to determine a structure of the correct symmetry, leading to consequences for their possible formation during the microphase separation transition from the isotropic melt.

A triangulated iso-surface of the proto structure can serve as starting point for the iterative minimization of an energy functional consisting of surface tension, elastic bending energy, and possibly other terms, leading to a realistic picture of the structure in the strong segregation regime. Two examples for minimized structures (double diamond and gyroid) are shown below.



A 3D Fourier transform of the minimized triangulated structure can be efficiently performed using the divergence theorem, i.e., by converting volume integrals into surface integrals leading to sums over triangles.

The resulting structure factor does not only determine the intensities to be observed in a scattering experiment but, making use of the appropriate theorems of the Fourier transformation, it can also be used to calculate the density projection in real space of a section of the structure of arbitrary orientation and thickness, as it can be observed by transmission electron microscopy.

This approach has considerable advantages compared to real space methods such as ray-casting through a simulated structure. For example, it is essentially analytic, and a finite width of the interface can be easily taken into account.

Examples for density projections in (111) direction are shown above on the right-hand-side of the figure (upper picture: double diamond, lower picture: gyroid).

ORDER - DISORDER TRANSITION IN SELF-ASSEMBLED COLUMNAR PHASE FORMED BY A POLYMETHACRYLATE WITH A HIGHLY TAPERED SIDE CHAIN AND ITS MONOMERIC PRECURSOR

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Insight into the supramolecular structure formed by a polymethacrylate with a highly tapered side chain is obtained from X-ray analysis of oriented fibers of the polymer and its monomeric precursor. The polymer is poly{2-[2-[2-(2-methacryloyloxy ethoxy)-ethoxy]-ethoxy] ethyl-3,4,5-tris (p-dodecyloxybenzyloxy) benzoate}; the monomeric precursor is the hydroxy-terminated side chain - 2-[2-[2-(2-methacryloyloxy ethoxy)-ethoxy]-ethoxy] ethyl-3,4,5-tris (p-dodecyloxybenzyloxy) benzoate. The polymer and precursor both form ordered solid state structures that are converted to columnar hexagonal liquid crystalline phases at approximately 40°C and 50°C respectively. The ordered solid state structures consist of ordered hexagonally packed tubular columns, in which the monomer units are probably packed with helical symmetry. For the polymer at 25°C, the column diameter is ≈ 60 Å with an axial repeat of 5.03 Å containing eight monomer units. For precursor at 25°C, the column diameter is reduced to ≈ 53.5 Å, probably due to the absence of the the polymer backbone from the center of the column, and the axial repeat is doubled to 10.04 Å. The X-ray data are compatible with a tighter winding of the monomers in a helical structure, but otherwise suggest that there are common features in the stacking of the aromatic groups in the two structures. The presence of polymer backbone causes the different temperature behavior of polymer and its monomeric precursor: hindered recovery of ordered solid state structures in polymer fiber and even the different sign of diameter changes with the temperature rising.

FIBROUS MANOCOMPOSITES BASED ON SiC WHISKERS

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The composite on the base of ceramic fine-dispersed nanolevel filler – SiC whiskers and thermal-resistant polymer binder was chosen as the subject of study in the present paper.

When analyzing the strength of fibrous fillers of the same SiC compound, whisker and continuous fibers, differing by 100 times in cross section area, the scale strength dependence is observed the positive manifestation of which is associated with the probability decrease of dangerous defects location on the specimens surfaces or inside them with their sizes decrease.

The SiC fibers strength with the diameter of 20 μm is 1500–2000 Mpa while the whiskers strength with the size of 0.2–0.3 μm approaching is in the range of 20000–25000 Mpa.

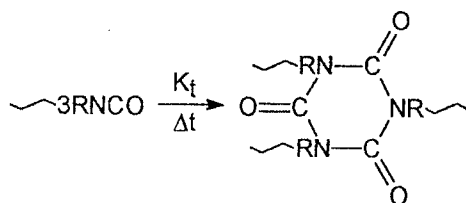
The binder and filler interaction nature is changed depending on filler sizes. The binder is uniformly distributed on the whiskers surface while the interaction between SiC fibers and binder is fully absent, that depends on the produced composites properties. In case of using the nanolevel objects the matrix monolithic structure formation process is observed on the developed surface of ultrafine filler with increasing the initial characteristics as compared to SiC continuous fibers by 5–6 times (15 and 3 kgf/mm^2 , respectively) not taking into account the porosity the first one.

The nanocomposites strengthening mechanism is due to restraining the globular matrix formations growth by nanoparticles, the effects of high surface energy and total interface extent on the structurized matrices in microvolume and also to changing the failure mode and microcracks by nanoreinforcement. As a result of this the expected increase of fatigue strength, stress rupture and cracking resistance takes place.

THE POLYURETHANEISOCYANURATE MORPHOLOGY

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The morphology of polyurethaneisocyanurates was studied by Gel Penetration and Reverse gas chromatography R-rays-structural analysis and IR-spectroscopy methods. Polyurethaneisocyanurates were obtained with olygoesters on the base of adipinic acid and ethylene- or ethylenebutyleneglycols, with molecular weight 2000. The formation of polyurethaneisocyanurate network structure by catalytic self-assembly of toluenediisocyanate proceeds according to following scheme:



For this, aminophenols of different kind of structure and degree of basicity have been used as coordinating catalysts which also promote urethane and allophanate reactions along with trimer formation. Therefore, polyurethaneisocyanurate network structure contains the spectrum of the same bonds. Polymer morphology substantially depends on the content of the mentioned groups which may vary according to isocyanate:olygoesters:coordinating catalyst ratio.

It was showed that common statements concerning the occurrence of flexible and rigid fragments in polyurethane structure are confirmed only in part. It is particularly referred to polymers obtained with high "isocyanate index". In the case, it was also detected that diisocyanate trimer passes into separate phase. X-rays-structural analysis gives the picture of stellate polymers with strongly pronounced isocyanurate homopolymer fragments. This reflects on polyurethaneisocyanurate properties resulting in abrupt increase of the yield temperature and hardness.

MULTIPLETS IN TELECHELIC POLYMERS: MOLECULAR DYNAMICS SIMULATION

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In the last time a great attention has been paid to the investigation of associating polymers containing hydrophobic, polar or ionic groups which strongly attract each other. Due to this attraction such polymers are capable to associate and form the multiplet structures. One of the simplest examples of associating polymers is the so-called telechelic polymer with dipole groups at the both ends of flexible chain.

We present the results of the molecular dynamics computer simulation of equilibrium multiplet structures formed by telechelic polymers. We study the dilute and semi-dilute solutions of telechelic chains. The interaction between internal links is described by repulsive part of Lennard-Jones potential that mimics an athermal condition. The interaction between terminal links is modelled by Lennard-Jones potential with strongly attractive part. It is found that under some conditions spherical micelles can be formed with core consisting of terminal links. The dependencies of various properties of micelles (mean size and shape, aggregation number etc.) on polymer concentration and temperature are obtained and compared with theoretical results.

For concentrated system the static structure factor was calculated. It shows that in such system in the limit of the strong segregation the microdomain structure of micelles' cores is formed.

SIMPLE ONE-PARTICLE DIFFUSIONAL MODEL TO MIMIC SOME PROPERTIES OF THE GLASS TRANSITION

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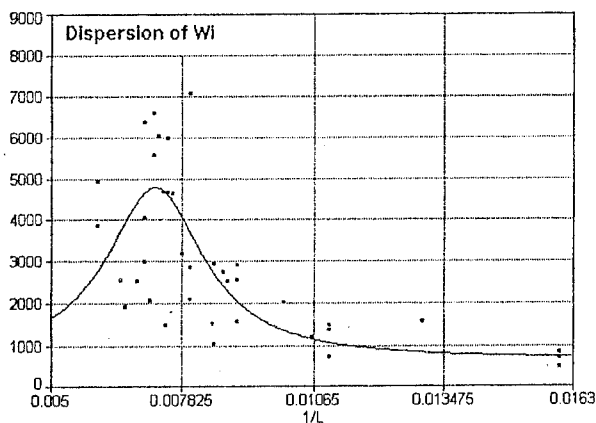
A new simplified model is proposed to mimic some properties of the glass transition. The physical system undergoing glass transition is modelled as Brownian particle diffusing in one- or two-dimensional space with obstacles. In one dimension obstacles are points which cannot be crossed by Brownian particles, in two dimensions obstacles are randomly distributed sections of straight lines which are impenetrable for the diffusing particle. The obstacles have a finite lifetime τ . After time τ the obstacle disappears and reappears in some new random position. In another modification of the model the obstacle-barrier can be opened for short time and then closed again. Both cases are studied for one-dimensional diffusion, while in two dimensions only the first modification of the model is considered which makes it potentially applicable to the properties of glass transition. The main feature of the model is that the mean lifetime of obstacles τ is connected with the diffusion coefficient of the Brownian particle through the coupling equation $D\tau = K$, with K being the coupling constant. Both analytical calculations and results of computer simulations are presented. The model is shown to reflect some of the physical features of real glass forming liquids. It was found that a slight change in the model, i.e. opening and closing of a barrier in the same position versus transfer of a barrier to a new position, leads to a drastic change in the diffusion kinetics of the system.

MONTE CARLO SIMULATION OF LARGE-SCALE (MESOSCOPIC) HETEROGENEITIES IN CROSS-LINKED AND ASSOCIATIVE NETWORKS

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Using the so-called bond fluctuation model we performed Monte Carlo simulations of the polymer gels and networks formed under different conditions at solid surface. The first method of network preparation is based on irreversible condensation of *tri*- and *di*functional monomers. In the associative networks, the chemical bonds between the same monomers may open and close in a dynamic equilibrium. In both cases, the reaction, when proceeding for long times, leads to branched objects in which *tri*functional monomers become branch points. Our study concentrates on those quantities which are most sensitive to structural and topological properties on all length scales. As a measure of spatial fluctuations of the cross-linking density we use the static structure factor $S(q)$. Well pronounced difference in $S(q)$ obtained by the time and ensemble averaging procedures demonstrates the *non-ergodic* nature of randomly cross-linked networks in the low- q region, i.e., at the mesoscopic length scale ($L \sim 10^2$ monomer units). The spatial heterogeneities become larger for overswollen or collapsed networks. The existence of such spatial heterogeneities is due to the competition between short-range excluded-volume



monomer-monomer interactions and an effective long-range attraction induced by chemical cross-linking. The topological properties of the networks manifest the sharp growth of their fluctuations at the same spatial scales. Greatest dispersion of the Wiener topological index, Wi , exhibits at $L \sim 10^2$ m.u., as it can be seen in Figure.

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FORMATION OF "FREE VOLUME" PHASE AT VITRIFICATION OF 2D LENNARD-JONES SYSTEM. COMPUTER SIMULATION

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Recently it was shown that the glass transition of the polymer system is possible at excess volume. Different explanations of that were suggested, but none of them was well-founded. In order to clear up this problem we carried out the molecular dynamics computer simulation of vitrification of very simple system by cooling it at the constant pressure or at constant volume.

This system consists of 500, 1000 and 5000 Lennard-Jones disks of two different diameters and masses on plane. The glass transitions were founded in all cases. This has been confirmed by mechanical behaviour of the system and disappear of the diffusion processes. Besides, vitrification at constant and excess volume occurred together with another phase transition: discharge volume excess in independent new phase - emptiness. Big density fluctuations are formed in the cases; size of them depends on the condition of cooling. This results agree with the mathematical model of vitrification suggested earlier by Gusev, Bulatov and Oleynik.

TRANSPARENT MICROHETEROGENOUS BLENDS OF MULTIBLOCK COPOLYMERS WITH FOREIGN HOMOPOLYMERS

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The formation of transparent films cast from solutions of blends of a multiblock copolymer with a foreign homopolymer which is separately not compatible with each of the blocks of the copolymer is described. The fact that this phenomenon is rather in common is illustrated by the examples of blends of some flexible polymers (PS, PMMA, PVC) and semi-flexible cellulose triacetate with such multiblock copolymers as polycarbonate/poly(dimethylsiloxane), polysulfone/poly(dimethylsiloxane), polysulfone/polybutadiene, poly(tetramethyleneoxide)/polybutadiene, ladder polyphenylsilsesquioxane/poly(dimethylsiloxane). Transparent blends were found to form at concentration of block-copolymer in the blend up to 10 weight % and at certain compositions of each type of the block-copolymers. An obligatory prerequisite to the formation of transparent blends is compatibility of the copolymer and homopolymer in a common solvent. Some phase diagrams of ternary systems homopolymer- block-copolymer- solvent and diagrams showing the translucence of the above blends as a function of their composition are given.

Using electron microscopy, DMA, TMA and radiothermolumene-scence techniques it was shown that the transparent blends are two-phase systems and their transparency is connected not with the genuine thermodynamic compatibility of the both blend components but with a very high degree of dispersion of the block-copolymer phase. This trend of the block-copolymers of the certain compositions to disperse in the foreign homopolymer up to nano-dimensional particles is discussed in the terms of hindrances to the full phase separation in multiblock copolymers and the influence of different interactions of the homopolymer macromolecules with two types of blocks in each copolymer on this process.

THE THEORY OF SUPERSTRUCTURES IN BLOCK COPOLYMER SYSTEMS

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Phase diagram in pure diblock copolymer and diblock copolymer - homopolymer mixtures was calculated in strong segregation regime. In this regime A and B blocks of diblocks and B blocks of homopolymer are good separated on the three different regions with thin interface. Free energy of this mixture for a given symmetry of elementary cell is a function of only two parameters: diblock copolymer composition f and volume fraction of homopolymer ϕ .

For fixed f and ϕ , and a given structure symmetry the free energy is a functional of the shape of interfaces between A and B blocks and between the diblock and homopolymer. Most of the existing models assume that the interfaces are spheres, cylinders or other surface of constant mean curvature. In our approach the shape of these interfaces is not predefined but rather is found from the condition of free energy minimum.

Another assumption, which was often used, is the assumption of a round elementary cell for cylindrical and spherical structures. We show, that for $\phi \sim \frac{1}{2}$ this assumption can not be used for precise calculations, which are necessary for a study of OBDD and other bicontinuous phases. So we do not use this assumption, and obtain the shape of interfaces for cylindrical, spherical and OBDD morphologies.

The results for the diblock copolymer - homopolymer mixtures are presented in a phase diagram (Fig.1) in coordinates f and ϕ and as a dependence of the free energy on f for fixed ϕ (Fig.2). The case $\phi = 0$ correspond to pure diblock copolymer system, which we have investigated in a pervious work.

The presented scheme of calculations can be used to test the stability of other new superstructures, such as gyroid, modulated lamellar and others.

Conformations of star-branched polyelectrolytes

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March 1, 1995

The scaling theory describing the conformations of weakly charged star-branched polyelectrolytes in dilute and semi-dilute salt-free solutions is developed. The dependence of the star size on the number of branches as well as on the solution concentration is analyzed. It is shown that the star size increases with an increase in the number of branches, f , at a small f and tends to a constant value at large f . An increase in the concentration of stars in the solution results in a decrease in the star size R according to the power law: $R \sim c^{-1/3}$ in the range of moderate concentration and $R \sim c^{-1/4}$ at larger concentration. For stars with a small number of branches the behaviour $R \sim c^{-1/2}$ in a certain concentration range is also predicted. The collapse transition which occurs in the polyelectrolyte star if the solvent strength decreases is also considered; it is shown that the collapse of the star with a small number of branches is accompanied by the loss of the star spherical symmetry.

THE STUDY OF NATURE OF THIOKOL-EPOXY POLYMER AND BRASS
SUBSTRATE INTERPHASE LAYER
WITH EPR AND ELECTRON SPIN ECHO.

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The conditions under which hermetics can be used largely depend on the nature of the bond between the polymer and the substrate. In this report results of the study of thiokol-epoxy polymer and the brass substrate interphase layer with EPR at the room temperature and with electron spin echo (ESE) at temperatures 1.6-4.2 K in X band are presented. To study the depth of penetration of Cu(II) ions in the hermetic the EPR tomography was used. The EPR spectrum of species from the interphase layer have been measured and assigned to the bivalent square copper ion complex, sulfur-containing fragment being the ligands. The EPR signal intensity dependence on the free sulfur content in the hermetic was found to be opposite to the adhesion values.

The analysis of distance between the external half-intensities of the EPR signal in gradient field allows one to find the depth of the maximum penetration of Cu(II) ions from the surface as 1 ± 0.5 mm.

The quantum chemical calculation have been made to interpret the experimental dependencies of adhesion strength on the content of free sulfur.

The temperature dependence of phase memory time was measured using the ESE method. It is not defined by spin-lattice relaxation and is typical for glasses. The two pulse echo decay was exponential though no any contribution of instantaneous diffusion was observed. This suggests that the copper complex has structure variations similar to glass ones. Preliminary results of the ESE modulation analysis suggest that protons are in the second coordination sphere of the Cu(II) ion.

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MACROMOLECULAR REACTIONS AS A TOOL TO CONTROL POLYMER BLEND STRUCTURE: SIMPLE THEORETICAL MODELS.

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Chemical transformations of blend components occurring directly during processing (reactive extrusion, reactive compatibilization) affect significantly the blend structure and, as a consequence, its properties.

So far a theory describing an evolution of a structure of reacting polymer blend under concert action of both the reaction and interdiffusion is hardly developed. The main difficulty to create such a theory is connected with irregular structure of the reaction products. Indeed, it is impossible to solve the problem without a development of non-equilibrium statistical thermodynamics of blends containing irregular copolymers.

In this paper we present a theoretical description of processes in reacting polymer blends in terms of linear non-equilibrium thermodynamics. We have applied Zubarev method of quasi-equilibrium statistical operator to derive the expression for free energy and variational approach to obtain the matrix of Onsager kinetic coefficients.

A simple model of reacting blend is considered. Irreversible macromolecular reaction (pendant groups are transformed, the backbone being unchanged) with accelerating interchain effect proceeds in a blend of compatible polymers A and B. The theory permits to describe the blend structure in details including a spatial distribution of reacting and non-reacting macromolecules, that of transforming units and a dispersion of compositional heterogeneity of reacting chains. An influence of various factors on the blend structure is discussed.

Also another model is considered: the formation of block-copolymers due to reaction between end-groups of the blend components. In that case the theory describes an evolution of the structure as a result of competition between spinodal decomposition and compatibilization during block-copolymer formation.

FORMATION OF FROZEN MORPHOLOGY ON NANOMETER SCALE IN BINARY BLENDS: COMPUTER SIMULATION OF MICROPHASE SEPARATION

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The study of the formation of microheterogeneity on a nanometer scale in A/B blends has been of considerable theoretical and technological importance in order to develop new materials with specific properties. Recently intensive interest has been paid to the problem of the microphase separation in binary systems with the A component which is glassy in the bulk state. In this report, we present a simple computer model for Monte Carlo and molecular dynamics simulations which should mimic some properties of A/B blends with glassy A component.

We consider a mixture of two molecules A and B interacting with each other by the repulsive forces (A-A, A-B, and B-B interactions are the same, i.e. the mixture is athermal). The difference between the molecules A and B is in the "rules of motion" which we impose. Namely, the motion of the B particles is unrestricted (usual case). At the same time, let us assume that under some conditions the A particles become frozen because of glass transition. Conditions for the A particles motion are determined by the local concentration of particles, n , within some sphere of radius r^* .

Two different models were studied. In the case of "model of plastification" (P-model) the A particles were considered to be frozen if the local concentration $n(B)$ of particles B becomes lower than some critical value $n^*(B)$. In the second case referred to as "model of glassification" (G-model) the A particles are frozen if local concentration $n(A)$ is higher some threshold value $n^*(A)$. If the critical conditions are not fulfilled, the A particles move in accordance to usual laws.

Cases when the A and B components were either polymer or low-molecular molecules were studied. In all these cases switching of our "rules of motion" leads to the appearance of micro domain structures. The scale of these structures corresponds to ten-twenty microscopic sizes, i.e. to the several nanometers. It is found that the kinetics of cluster growth and the morphology of arising clusters differ essentially for two models and depend on the following parameters of system: the total densities of the A and B particles in system, the critical radius r^* and critical values of n^* .

Thus, it is demonstrated that the imposing of new nontrivial "rules of motion" in athermal A/B blends leads to microphase nano-separation and the formation of super molecular structures. It should be noted that fantastical shape of arising clusters and their amusing evolution makes the observation of micro domain growth as interesting as computer game.

PVA-CRYOGELS' MACRO- AND MICRO-HETEROGENEITIES INDUCED BY FILLERS OF VARIOUS POROSITY

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Poly(vinyl alcohol) cryogels - *cryoPVAGs* - are formed as a result of freezing-thawing the concentrated PVA solutions. These gels possess a high-porous morphology with pronounced macroand micro-heterogeneities, which depend on many factors including the polymer concentration in an initial solution, the solvent used, temperature conditions of the proper cryotropic gelation, etc. In addition to them, definite variations in the "architecture" of *cryoPVAGs*' supramolecular network can be induced by filling these materials with disperse porous and nonporous fillers.

The influence of the entrapment of three types of insoluble particles within PVA cryogels on their structure and properties was investigated. The fillers used were as follows: inorganic particles (silica of various porosity, controlled pore glass and non-porous powder titania), organic polymeric microbeads made from a cross-linked dextran (Sephadex gels of various cross-linking extent), fillers of biological origin (viable and modified yeast cells).

It was recognized that one of the main peculiarity, determining the filler's activity regarding to *cryoPVAGs*, was the molecular-sieve properties of a discrete phase in respect to polymer in a continuous phase. Therefore, in the case of gellike fillers the highest reinforcing effect was inherent not to the most rigid filler but to that inducing some enrichment of PVA solution between the additive's particles with higher molecular weight fractions of the polymer due to their nonuniform partition among such a filler and a binder. This effect gave rise to an additional micro-heterogeneity of composite *cryoPVAGs* as compared to the non-filled ones. Electron microscopy studies revealed the fact of the formation of compacted cryogel regions near the surface of those filler particles, which did not allow PVA macromolecules to penetrate inside the grains, contrary to the less heterogeneous *cryoPVAG* structure near the surface of particles with higher pore sizes. Thus, similar differences reflected the variations in the macro-heterogeneity of these systems.

Other important moment was the possibility of formation the "network-in-network" structures within each insoluble particles. It was demonstrated that in the case of *cryoPVAGs* filling with porous mineral additives (pore size larger than PVA gyration diameter) or with artificially-perforated yeast cells, alike discrete particles have appeared to be "linked-in" the binder matrix, thus promoting considerable increase in the mechanical strength of a composite cryogel.

POLYMER-METAL NANO-COMPOSITES OBTAINED BY MATRIX RED-OX POLYREACTIONS

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Polymer-metal composites were obtained by reduction of metal salts (sulfates of Ni^{2+} and $\text{Ni}(\text{NH}_3)_6^{2+}$) in aqueous solutions of polymer matrices such as polyethylene oxide (PEO), poly-N-vinylpyrrolidone (PVP), polyacrylamide, polydimethyldiallylammonium chloride. According to electron microscopy and FMR data, obtained composites comprise zero-valent Ni particles with diameter 2-10 nm; the crystal lattice of Ni shown to be either face- or body-centered depending on the reaction conditions.

The composite suspensions show no Ni oxidation for several days or weeks; dried composites are stable on storage in air over several months. Catalytic activity of PEO-Ni composites in the reaction of hydrazine borane destruction was shown to be an order of magnitude higher than that of Ni particles obtained by the same way in the absence of polymer matrix as well as that of the mixture of the Ni particles and PEO.

The mechanism of polymer-metal composite formation is proposed. The mechanism includes the step of 'recognition' of growing metal nuclei by a matrix resulting in screening of nuclei surface by a macromolecule providing small size and high stability of metal particles. A simple mathematician model is proposed to describe size distribution of metal particles in the composites as a function of matrix MW and concentration, energy of polymer - particle and polymer - metal ion interactions. Conditions are estimated when the distribution is narrow.

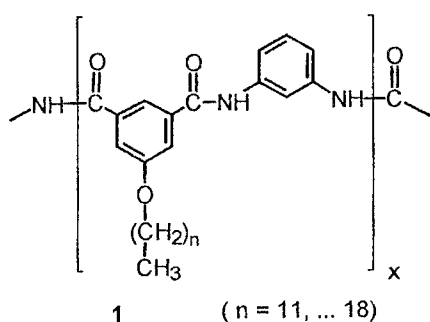
Acknowledgment. The research described in this publication was made possible in part by Grant № 93-03-18096 from the Russian Foundation for Fundamental Investigations and Grant № N2S000 from the International Science Foundation.

STRUCTURAL ORGANISATION OF POLYMER LATTICE USING HYDROGEN BONDS AND ALKYL CHAIN CRYSTALLISATION

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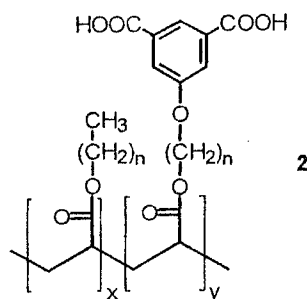
Design and synthesis of polymers with well defined structure and macroscopic organisation in the solid lattice has been an active area of research during the last decade. As an on-going research program on this topic in our group, several new synthetic concepts are pursued for structural organisation of polymer lattice using weak intermolecular interactions such as hydrogen bonding and van der Waals interaction. [1]



The first example involves the case of poly(isophthalamide) **1**, where interchain hydrogen bonding of amide groups present on the polymer backbone in combination with side chain crystallisation results in a layered structure. [2]

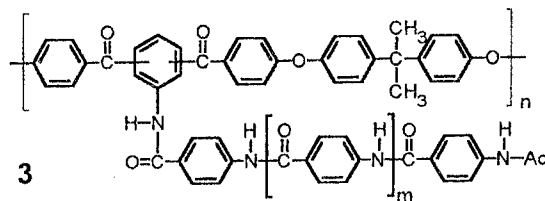
In the second approach homo polymerisation of acrylic group functional-

ised alkoxy substituted isophthalic acid and their copolymerisation with alkyl acrylates results a series of polymers **2**. The poster will discuss about characterisation and structural study of these polymers using a variety of techniques.



The third approach focuses on the influence of inter chain hydrogen bonding on the properties of various polyarylene ethers **3**. Polyether ketones grafted with oligo-peptides and carboxy-functionalised moieties are studied for change in their thermal and mechanical properties. [3]

In all the above mentioned cases the supramolecular structure of the polymer lattice is elucidated via temperature depended IR, X-ray and DSC measurements.



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- [1] S.Valiyaveetil, C.Gans, M.Klapper, R.Gereke, K.Müllen, *Polymer Bulletin*, **34**, 13 (1994)
- [2] S.Valiyaveetil, V.Enkelmann, K.Müllen, *J.Chem.Soc.,Chem.Comm.* 2097 (1994);
- [3] M.Klapper, A. Parthiban, U.Hoffmann, K.Müllen, *to be published*

Influence of the Solvent on Helical Structure of Isotactic Polypropylene. Molecular Dynamics Simulation.

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Isotactic polypropylene (PP) is commercially important polymer which has been studied extensively over the course of the last three decades. We report here the results of NVT molecular dynamics (MD) simulation [1] of i) one isotactic polypropylene chain plus solvent and ii) one molecule of 2,4-dimethylpentane (DMP) (as a low - molecular analog) in the same solvent. United-atom models with rigid bonds both for polymer (23 groups in main chain and 11 side groups) and for DMP molecule were used. Valence angles in both models are fixed with the help of harmonic bending potential. Torsion interactions are presented in the form proposed by Jorgensen et al [2]. Lennard-Jones potential was used to describe excluded volume interactions.

During computer experiment the statistical weights of every conformational state for the model of DMP have been calculated. For the model of DMP with rigid bonds and valence angles and in vacuum it is possible to calculate these statistical weights numerically with a precision controlled by the algorithm. One observe a strong solvent effect as the conformations of DMP molecule in MD are very different from ideal gas ones. Namely, in vacuum the most populated are two conformations - g^+t and tg^- . This fact leads to the two known helical structures for isotactic PP - the sequences of $(g^+tg^+t...)$ or $(tg^-tg^-...)$ conformers. In solution there are two conformations - tt and g^+g^- which are extremally populated in comparison with the situation in vacuum. DMP (and PP) molecule in solution becomes more oblate but two helical structures also present.

Results of MD simulation for the local dynamics of PP were compared with Hall-Helfand [3] and Monnerie et al [4] theoretical predictions.

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ASSOCIATIVE BEHAVIOR OF WATER SOLUBLE RIGID-ROD SULFONATED POLYNAPHTHOYLENEIMIDE

G.I. Timofeeva, I.I. Ponomarev, R. Mercier

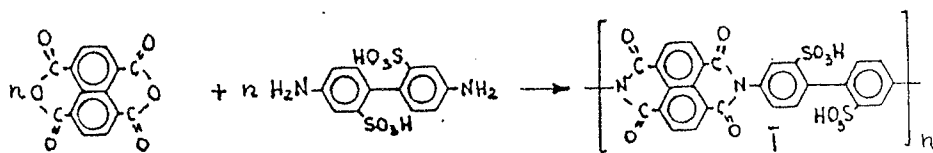
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Water soluble liquid crystalline polymers have received considerable interest in recent literature. The sulfonated derivatives of the rigid rod aromatic polyamides have been investigated to assess their polyelectrolyte properties and the ability to dissolve in water.

Polynaphthoyleimides occupy a particular place among other types of polyimides, since, besides high physico mechanical characteristics they display very good hydrolytical and chemical stability. So, we have tried to synthesize a new class of water soluble polyheteroarylene - sulfonated polynaphthoyleimide. The one of the possible ways to achieve that consists in the use of dianhydride of 1,4,5,8 - naphthalenetetracarboxylic acid and 2,2 - disulfobenzidine:



The synthesis of this polymer was the same as described previously. The structure of I has been confirmed by elemental analysis, FT-IR, NMR and RX investigation of the model compound.

Viscosity measurements of dilute solutions of I in water solution (the free acid form) are represented in Fig. 1. To gain further information regarding this aggregation effect we have studied the viscosimetric behavior of I in aqueous solutions at different pH values (Fig. 2). The Fig. 3 shows interesting viscosimetric behavior of aqueous solutions of I at different sodium chloride concentrations.

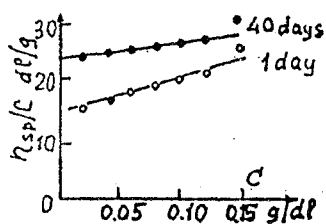


Fig. 1

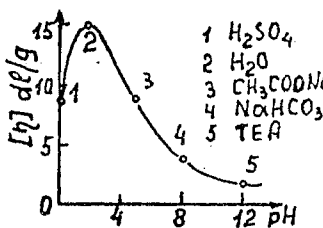


Fig. 2

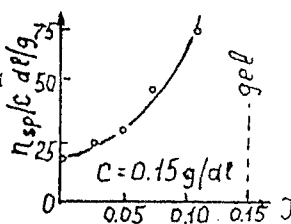


Fig. 3

Light scattering and sedimentation experiments confirm the suggested aggregation of I and consist in an increase in molecular weight of I without being substantially changed in different types of aqueous solutions. These aggregates could consist of very tightly packed rigid rods.

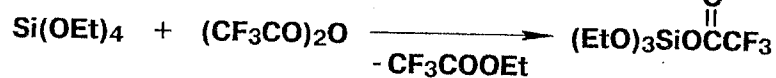
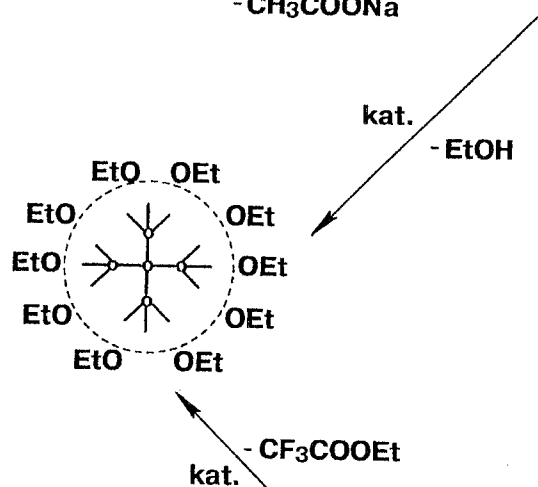
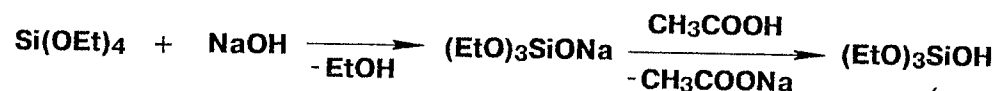
HYPERBRANCHED ETHYLSILICATE - INORGANIC POLYMER OF DENDRITIC STRUCTURE

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The synthesis of inorganic polymer of dendritic structure were elaborated with employing of tetraethoxysilane sodiumoxy or trifluoroacetic derivatives. Both of these monomers may be considered as A_1SiB_f monomers satisfied the Flory requirement for polymers of hyperbranched structure obtaining:



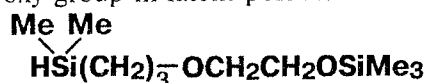
For identification of prepared multifunctional polymers most of functional groups were blocked by treatment of trimethylsilyltrifluoroacetic ester. This operation allows to get GPC data for treated ethylsilicates of dendritic structure. By hydrolisis of hyperbranched ethylsilicates in delute solutions it's possible to obtain hydroxy derivatives of this polymer which are soluble in polar solvents and stable for storage even at high concentration. New polymer may considered as a kind of sole of silica and may be employed as stable matrix for homogenous immobilization different chemical objects.

(This research was supported by the Russian Science Foundation, grant № 93-03-5736).

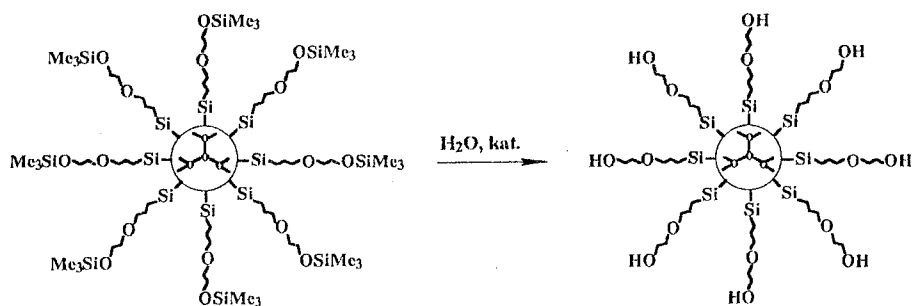
POLYCARBOSILANES OF DENDRITIC STRUCTURE. SYNTHETICAL APPROACH OF HYDROPHILISATION.

E.V.Getmanova, O.B.Gorbacevich, N.B.Chenskaya and A.M.Muzafarov
117393, Russia, Moscow, Profsoyuznaya st. 70, fax. (095) 420-22-29

Chemical nature of organosilicon polymers of dendritic structure are ideal for application in biomedical field. High chemical stability and functionality together with inertness and wide temperature range of potential application allow to consider these polymers as very promising objects of investigation. However, until the recent time our attempt of obtaining of hydrophilic derivatives of these polymers by chemical transformation of functional groups was failed. Majority of well-known processes of double bond interaction with different agents were accompanied by cross linking reaction. That's why we synthesized oligomer with hydroxy group in latent position:



This oligomer was employed for hydrosilylation of regular and unregular polyallylcarbosilanes of dendritic structure and may be considered as some universal agent of hydrophilisation of polymers with high concentration of unsaturated groups. After finishing of hydrosilylation process obtained polymers are readily hydrolyzed with poly-ols of dendritic structure formation.



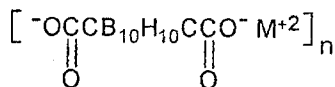
Some properties of these polymers and specificity of association of hydroxyl groups were studied and will be discussed.

(This research was supported by the Russian Science Foundation, grant № 93-03-5736).

HALATOPOLYMERS OF m-CARBORANEDICARBOXYLIC ACID FOR INTRODUCTION OF METALS IN THE FINE-GRAINED STATE INTO POLYMERS

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Halatopolymers of m-carboranedicarboxylic acids next structure:



M = Mg, Ca, Mn, Cu, Zn, Sn, Cd, Ba, Pb, Co, Fe
were first obtained and investigated.

It was determined that halatopolymers of m-carboranedicarboxylic acid differ from halatopolymers of organic dicarboxylic acid by infusibility, solubility in the water and reducing power at high temperatures.

The ability of Cu, Cd, Pb, and Sn-halatopolymers to produce unoxidized metals in polymers by heating have been shown.

The dimensions of obtaining free metal particles depend on the temperature treatment and lie in the range between 5–30 nm.

SYNTHESIS OF METAL-CONTAINING OLIGOMERS AND POLYMERS ON THE BASIS OF OLIGO- AND POLYARYLENES AND ATOMIC METALS

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A number of oligomers and polymers have been synthesized by low-temperature interaction of atomic metals and ultradisperse particles (UDP) of the metals in solvents with polymeric matrices including high-molecular weight compounds at the point of their formation.

The following polymers and oligomers of the oligoarylene type are used as macro-molecular matrices: oligobenzyl, the branched oligophenylene, linear oligophenylenes - copolymers of benzene with toluene, benzene with m-xylene, poly-p-xylylene (PPX) and others. For comparison polystyrene is also used. As atomic metals Cr and Fe were used. The polymers were prepared in a reactor of the stationary type.

It is found that the interaction of Cr with polymeric matrices leads to formation of metal-containing oligomers and polymers with the metal particles of the cluster type (from 3 to 20 nm). It is shown that the macromolecular matrices participate in formation and stabilization of the clusters.

During the condensation of atomic Cr and Fe on PPX at the point of its formation the obtained polymeric structures contain the cluster particles more than 3 nm in size evenly distributed in the polymer bulk.

The synthesized metal-containing oligomers and polymers reveal the electroconducting and catalytic properties.

THE PHASE TRANSITION TEMPERATURES OF THE THIN LIQUID
CRYSTALLINE FILMS CAPSULATED IN POLY-PARA-XYLYLENE.

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119899, Russia.

Liquid crystalline thin films are of great interest due to their properties, different from the properties of liquid crystalline bulk substances.

Liquid crystalline films capsulated in poly-para-xylylene have been obtained by layer deposition of reagent vapours (liquid crystal and para-xylylene) on cooled by liquid nitrogen copper surface and following polymerization of p-xylylene by heating.

The liquid crystalline substances we used were:
4-amy1-4'-cyanobiphenyl (5CB) with mesophase existence temperature range from 21 to 36°C and 4-methoxy-benzyldene-4'-butyl-aniline (MBBA) with mesophase existence temperature range from 21 to 47°C.

The metallization of polymer have been made by Ag atoms deposited on the cooled samples. The beam of Ag atoms have been obtained by evaporation of metal Silver in high vacuum conditions.

The thickness of obtained liquid crystalline films were about 2-5 micrometers.

To identify phase transitions produced films were analized by optical-polarized microscopy method. Transitions from nematic to isotrop phases were revealed by this method only for metallized samples: 26°C for 5CB (36°C - for bulk substance) and 31°C for MBBA (47°C).

Another mode to identify temperature of phase transition in 5CB films was ESR-method. The stable radical TEMPO was solved in liquid crystal before vacuum deposition. Concentration of TEMPO was about 0.1M. As a result phase transitions have been revealed independent of metallization of samples.

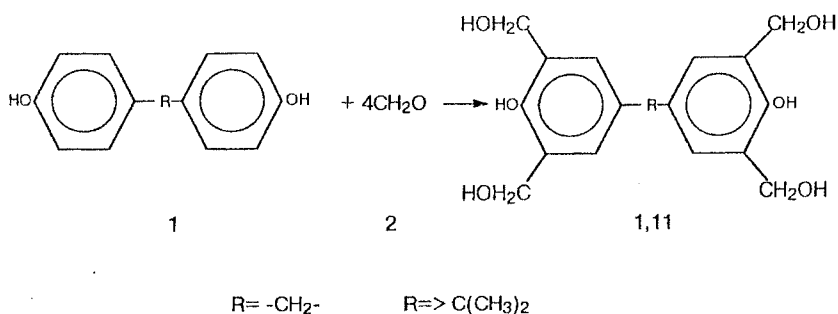
The results are discussed.

NANO-ARCHITECTURE of POLYMETHYLENPHENOLES. SYNTHESIS AND PROPERTIES.

I.I. Tverdokhlebova, W.K. Schitikov, N.N.Kudryavtseva, V.A. Sergeev.

INEOC RAS, 117813, Moscow, Vavilov str. 28.

New chemical approach to step by step molecules construction has been worked out. To obtain the new olygomers of regular structure, architecture and molecular weight desired, molecules (I, II) - methylol derivatives of phenoles should be developed at the initial stage of bisphenole (1) and formaldehyde(2) synthesis-condensation.



Nano-architectures I and II are the basis for developing of more complicated nano-architectures (III), that can be used as the basis for the following three-dimension structured polymers of high order set structure, and so on (III-VI).

The structures of polymethylenphenoles molecules are confirmed at every stage of synthesis by chemical analysis, YMR and IK spectres, GPC, Mn.

As it is shown, in the presence of catalyst (HCl) olygomers with monomodale MMR, Mn,ms=Mn,cl are developed. Catalyst absence leads to the bimodale MMR, Mn,ms ≠ Mn,cl molecules developing.

Such olygomers with precise designated molecules structure and MM are of great importance for practical and ecological problems solving.

ANOMALOUS MICELLIZATION OF MULTIBLOCK COPOLYMER IN SELECTIVE SOLVENT.

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Association of multiblock copolymer polysiloxaneurethane-polycarbonate ($M_w = 40\,000$) has been studied by light scattering, viscometry and sedimentation analysis. This copolymer in benzene (selective solvent for polysiloxaneurethane block) forms polymolecular micelles having a polycarbonate core and a polysiloxane shell.

In this work we report results of our investigation of anomalous micellization phenomenon in certain concentration interval. As seen in Fig.1 the intensity of scattering light increases dramatically with increasing concentration, the dissymmetry $-Z$ passes a distinct maximum. In initial stage the insoluble block form the large particles with loose structure which are transformed to compact spherical micelles with increasing concentration. In region III ($C > 1.4$ g/dl) the solution have typical bluish opalescence, the dissymmetry is close to unity, the micellar mass is about $2 \cdot 10^6$ and radius of gyration is 20 nm. In the same region gradient curves obtained by method of sedimentation in ultracentrifuge show one peak ($S_c = 2.5 = 3.3 \cdot 10^{-13} \text{ s}^{-1}$, $D_c = 2.5 = 2.0 \cdot 10^{-7} \text{ cm}^2 \text{ s}^{-1}$). At the concentration $c = 0.5$ g/dl (region II) sedimentation diagram shows two peaks (Fig.2) corresponding to two components: the "fast" peak with $S = 2.3 \cdot 10^{-13} \text{ s}^{-1}$ corresponds to anomalous micelles, the "slow" one with $S = 3.6 \cdot 10^{-13} \text{ s}^{-1}$ true micelles.

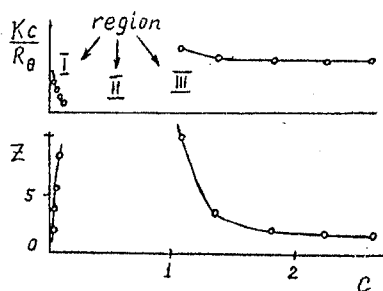


Fig.1

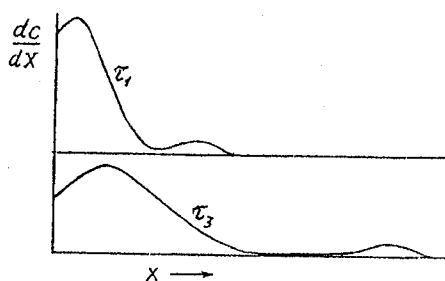


Fig.2

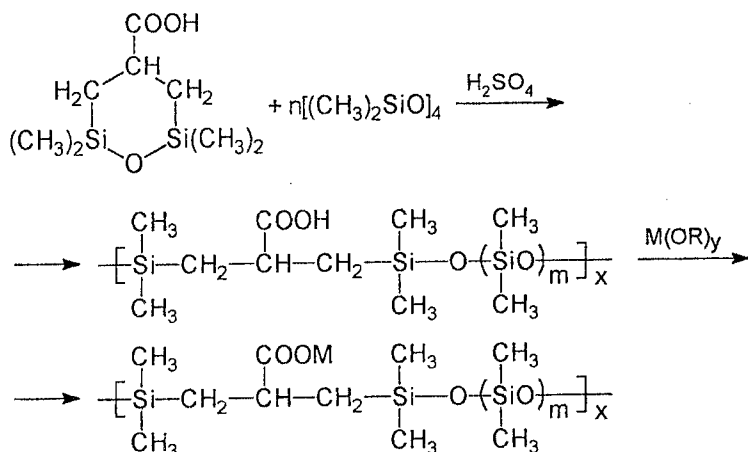
Thus we succeeded to discover the concentration interval of the coexistence true and anomalous micelles and to obtain their characteristics.

This research was supported by the Russian Science Foundation grant N 95-03-08558a

NOVEL SILICIUMORGANIC POLYMER SYSTEMS WITH STRONGLY ASSOCIATING GROUPS

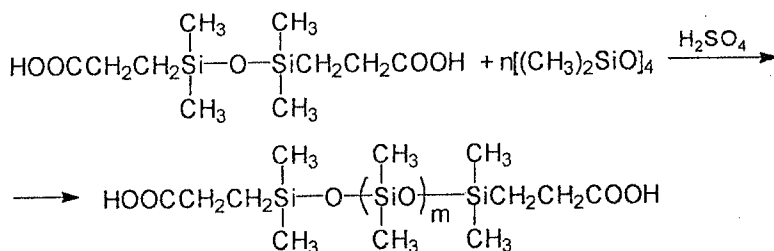
O.I.Shchegolikhina, I.V.Blagodatskikh, T.A.Larina, A.A.Zhdanov
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Polydimethylcarbosiloxanes, containing carboxyl and metallocarboxylate groups have been synthesized by cationic polymerization of octamethylcyclotetrasiloxane with oxadisilacyclohexane acid according to the following scheme:



M = Li, Zn; R = H, Ac; y = 1, 2

By the cationic polymerization of octamethylcyclotetrasiloxane with bis-(carboxyethyl)tetramethyldisiloxane the telechelic polydimethylsiloxanes with carboxyl group have been obtained:



Their consequent neutralization with metal salts leads to the formation of ion-containing polydimethylsiloxane telechelics.

These polymers manifest a tendency to the association and formation of micellar solutions and gels in nonpolar solvents.

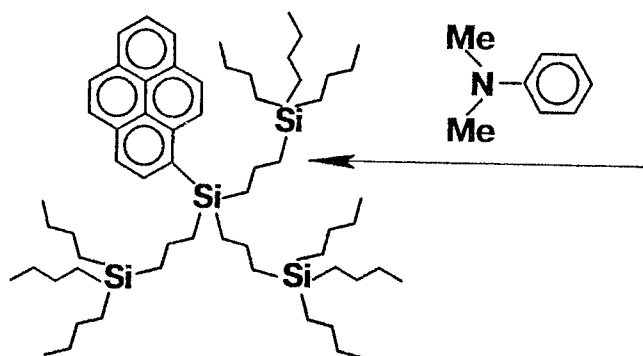
H-form of polymers can give molecular or micellar solutions depending on the preliminary treatment of samples.

FLUORESCENTLY LABELED ORGANOSILICON DENDRIMERS AND QUANTITATIVE ESTIMATION OF FILLING DENSITY OF DENDRITIC STRUCTURES.

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It's known the filling density of layers in dendritic structures increases with growing of number of generation and molecular mass. For quantitative estimation of this parameter carbosilane and carbosilanesiloxane dendrimers having a fluorescent mark (pyrene) on the central silicon atom have been synthesized by convergent and divergent schemes:



Measured kinetics of quenching of pyrene fluorescence allowed us to calculate the diffusion coefficients of the quencher to the fluorescent centre in the dendrimers of various molecular masses. Taking into account low concentrations of studying solutions of the dendrimers (10^{-6} mol/l) decreasing of the diffusion coefficients of the quencher with growing of molecular mass of the dendrimers may be considered as a quantitative measure of the external layer density of the different generation dendrimers. The influence of nature of solvents on the filling density of the synthesized carbosilane dendrimers was studied too.

This research was supported by the Russian Science Foundation, grant № 93-03-5736.

MACROMOLECULAR DESIGN in POLYCONDENSATION

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The problem of macromolecular design in polycondensation connected directly with a purpose of obtaining polymers with a desired complex of properties is one of the fundamental tasks of polymer chemistry.

The present report deals with our results in the field of nonequilibrium polycondensation macromolecular design connected with various distributions of comonomers and asymmetric monomers in polymer chains. In this study it was shown that:

- if all starting monomers are in solution at the beginning of polycondensation a polymer with almost statistical unit distribution is formed. Slight deviation of statistical microstructure in some cases can be explained by a marked dependence of the activities of the functional groups of intermonomer (symmetric monomer);

- the step introduction of comonomers in the reaction is not sufficient to produce block-copolymers. In the conditions of one-stage polycondensation the gradual introduction of intermonomer (symmetric monomer) in a solution of comonomers leads to a formation of block-copolymers (regular polymers with "head-to-head", "tail-to-tail" configuration). The length of blocks and the degree of randomness of copolymers obtained depend on difference in comonomers reactivity;

- the transfer from one-stage polycondensation to two- and stage-by-stage polycondensation expands the possibilities of polymer synthesis and enables to obtain block-copolymers with the desired blocks length.

MICELLIZATION OF BLOCK COPOLYMERS IN THE SUPER STRONG SEGREGATION LIMIT

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Amphiphilic polymers can self-assemble into a large variety of microstructures. Compared to low molecular weight surfactants, microstructures formed by polymeric amphiphiles are very stable and can be used for a number of interesting applications.

We investigated the formation of polymeric micelles of a series of Poly(styrene-*b*-4-vinylpyridine) (PS-PVP) block copolymers in toluene, a selective solvent for the PS-block. We find the aggregation number Z of the micelles to scale as $Z \propto N(PVP)^2 N(PS)^{-0.8}$, where N is the degree of polymerization of each block. This is in good agreement with theoretical predictions of Zhulina and Birshtein for micellization in an intermediate regime between "starlike" and "crew-cut" micelles, where micelles with high coronal segment densities are formed. The N^2 -dependence is a characteristic signature of the super strong segregation limit (SSSL), which has recently been predicted by Khokhlov et al. The strong N -dependence is caused by geometrical constraints imposed by a minimal surface area A per chain on the micellar core. This is in direct analogy to the self-aggregation of low molecular weight surfactants, where the head group area A' controls the aggregation number.

Such strongly segregated micellar systems are highly stable and allow a variety of applications. Inorganic salts can readily be solubilized into the micellar core. Micelles can then be used as microreactors: Reduction of solubilized metal salts (Ag, Au, Cu, Pd, Co) leads to the formation of nanometer-sized colloidal metal particles that are stabilized inside the micellar core. Group Ib-metals show a characteristic plasmon resonance in their UV/Vis-spectra, whose peak wavelength decreases with decreasing particle size. Similarly, nanometer-sized semiconductor particles (CdS) can be prepared. Such particles show quantum-size effects, i.e. the band gap increases with decreasing particle size as evident in a shift of the absorption edge in the UV/Vis-spectra. Micelle-stabilized Pd particles catalyze hydrogenation reactions with high selectivity and conversion. For example, dienes (cyclohexadiene, cyclooctadiene) can be selectively converted into olefines.

On texture and Laplacian growth by gas phase cationic polymerization

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Polymerization of organic precursors such as thiophene, benzene, furan, and naphthalene in glow discharges produce dense, homogeneous films with excellent linear and nonlinear optical properties (e.g. *Appl. Phys. Lett.*, **61**, 34 (1993)). The dynamics of the deposition process rely on positively charged molecular ions that are accelerated through a space-charge sheath to a substrate surface. Although the sheath dimensions are typically millimeters, one finds surface texture on a nanometer scale as a result of the local electric fields produced by gradients in the charge density at the electrically floating substrate. These gradients give rise to transverse electric fields that focus the impinging ions and thereby alter the local growth rate. The strength of these fields is proportional to the local surface curvature, so that the Laplacian growth analysis of crystallization first proposed by Mullins and Sekerka (*J. Appl. Phys.*, **34**, 323 (1963)) may be critically tested. We characterize the surface texture of a growing film by atomic force microscopy and analyze its thickness with spectroscopic ellipsometry. We find that the surface roughness increases exponentially with film thickness, in accordance with the *ansatz* of Mullins and Sekerka. Furthermore we find that the wavelength scales for the surface texture are not random; there is a range of spatial frequencies which experience stable growth, also in accordance with the Laplacian analysis. We will discuss the technological implications of these results on electrostatically modulated polymerization and the synthesis of nanometer-sized particles in dusty plasmas.